



Review

Heterogeneous Fenton catalysts based on clays, silicas and zeolites

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ARTICLE INFO

Article history:

Received 7 May 2010

Received in revised form 25 June 2010

Accepted 6 July 2010

Available online 15 July 2010

Keywords:

Heterogeneous catalysis

Clays

Zeolites

Mesoporous silicas

Pollution remediation

ABSTRACT

This review focuses on the use of layered and porous aluminosilicates and layered double hydroxides as catalysts for the Fenton reaction. In the general sections of this review we present the elementary equations leading to the generation of hydroxyl radicals from H_2O_2 and the subsequent reactivity of this highly aggressive species. After justifying the advantages of using insoluble solids as heterogeneous catalysts, replacing soluble iron salts, we discuss the desirable features that should have an ideal Fenton catalyst and which are the parameters to be considered when ranking the efficiency of the materials. The main part of this review is focused on presenting the results reported up to late 2009 obtained using layered and porous aluminosilicates as heterogeneous catalysts. The structure of these materials is briefly presented to highlight the benefits and advantages of each type of solid with respect to their use as catalysts. When presenting the catalytic data, special emphasis is made on the missing data that would be useful to clarify, the relative efficiency and performance of the materials. In the final concluding remarks we stress again that the present situation needs to be clarified to draw solid conclusions on the relative performance and efficiency of the tested catalysts.

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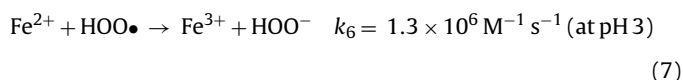
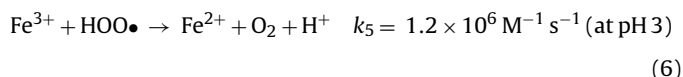
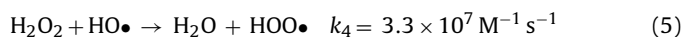
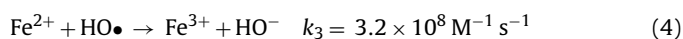
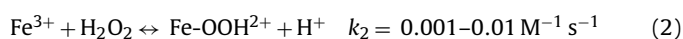
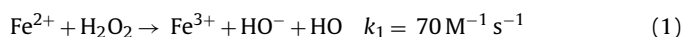
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1. Introduction

The Fenton process consists in the reaction of Fe^{2+} species with H_2O_2 under strong acid conditions to generate highly reactive hydroxyl radicals (HO^\bullet) [1–4]. The simplest Fenton process can be performed by reacting FeSO_4 with H_2O_2 in aqueous sulphuric acid solutions. Eq. (1) presents the stoichiometry of the process and the products formed.

As it can be seen there, Fenton reaction consists basically in the oxidation of Fe^{2+} to Fe^{3+} effected by H_2O_2 as oxidant. The important mechanistic feature of the Fenton reaction is that in the outer-sphere single electron transfer from Fe^{2+} to H_2O_2 generates hydroxyl radicals and hydroxide anions [2,3]. Concomitantly to the genuine Fenton reaction, other processes as those indicated in Eqs. (2)–(7) can also simultaneously take place [4–7]. These parallel processes are typically considered as undesirable, because they represent a wastage of H_2O_2 without leading to hydroxyl radicals.

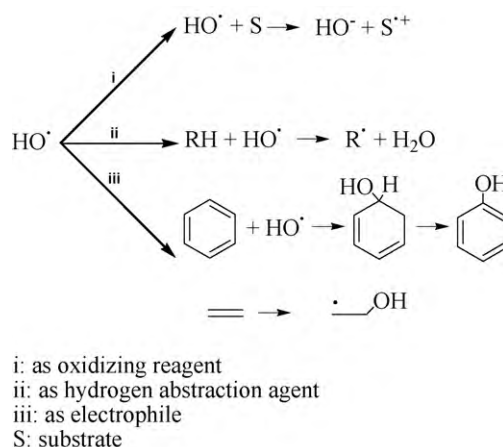


Besides iron salts, other transition metals that exhibit at least two oxidation states such as copper, ruthenium, cerium and manganese can also promote the generation of hydroxyl radicals from H_2O_2 [8–13]. However, due to economic and environmental concerns, iron salts are usually the preferred chemicals for the process.

Hydroxyl radicals are after fluorine atoms the most oxidising chemical species [4,14]. They are extremely powerful species to abstract one electron from an electron rich organic substrate or any other species present in the medium to form hydroxide anion. The oxidation potential of hydroxyl radicals has been estimated as +2.8 and +2.0 V at pH 0 and 14, respectively [14–16]. In addition to the reactivity as oxidising reagent, hydroxyl radicals can also abstract one hydrogen atom from hydrocarbons and other organic substrates [17–19]. The condition for hydrogen abstraction is that the hydrogen bond to be broken has to have a bond energy lower than 109 kcal mol⁻¹ that is the energy of the H–O bond formed in the process. Considering that the O–H bond energy is higher than most C–H bond energies, thermodynamics predicts that hydroxyl radicals should be able to abstract one hydrogen from almost every C–H bond in any organic compound [4,19,20]. The high oxidation potential of HO^\bullet and the high O–H bond energy ensures that HO^\bullet radicals is a general reagent able to attack virtually to any organic compound.

In addition, there is a third possible reaction pathway available to hydroxyl radicals consisting in the attack of HO^\bullet to multiple bonds [19]. Particularly, HO^\bullet can behave as strong electrophile attacking the Π clouds of aromatic compounds, alkenes and other unsaturated organic compounds [4]. Scheme 1 depicts the general reaction pathways available to HO^\bullet [4–7,21–23].

The high reactivity of HO^\bullet ensures that it will attack a wide range of organic compounds [19,24–26]. When performing the Fenton

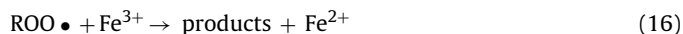
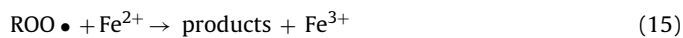
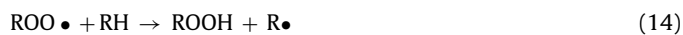
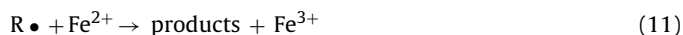


Scheme 1. General reactivity of hydroxyl radicals.

reaction under aerobic conditions, the initial attack of HO^\bullet renders carbon centred radicals, triggering a multitude of subsequent steps consisting in the trapping of carbon centred radicals or organic radical cations by molecular oxygen with the formation of organic peroxy intermediates [18,27,28] (Scheme 1). These intermediates after hydrogen abstraction will form organic hydroperoxides that under strong acid conditions (typically required for the Fenton reaction) decompose forming oxygenated products, generally alcohols and ketones [4,28]. When an excess of Fenton reagents is present, the primary compounds arising from one cycle of HO^\bullet attack, oxygen trapping, decomposition can undergo a cascade of secondary reactions leading to complex reaction mixtures having increasing oxygen content. Eventually some C–C bonds break and the original compound undergoes degradative oxidation giving rise to oxidized products with smaller number of carbon atoms. When fragments of one single carbon atom are formed the final Fenton reaction gives rise to CO_2 and the heteroatoms also form the corresponding oxygenated species such as NO_x , SO_x and PO_x . Formation of CO_2 and other oxides of a single central atom are generally termed as *mineralization*, meaning that the carbons and heteroatoms of the organic substrate are converted to inorganic species [29,30]. Eqs. (8)–(16) also illustrates the cyclic processes occurring in Fenton chemistry under aerobic conditions leading to the formation of CO_2 .



i: radical generation and oxygen trapping; ii: several steps



As it can be concluded from the above comments on the reactivity of HO^\bullet radicals under aerobic conditions, the Fenton reaction can be considered as a general tool to effect the degradation, and eventually mineralization, of organic compounds. In this context and particularly considering that from the environmental point of view organic compounds present in air and water are considered as pollutants, originating undesirable consequences for the environment, the most important application of Fenton chemistry is the

remediation of organic pollutants in water and soils [25,26,31–36]. However, the high reactivity of HO• can also be used to obtain valuable chemicals rather than to effect the degradation of organic compounds. From the synthetic point of view, the reactivity of hydroxyl radicals is extremely difficult to be controlled and for this reason product selectivity using Fenton is typically low, limiting considerably the interest of this reaction in organic synthesis [37]. For this reason, this application of Fenton chemistry to the synthesis of organic compounds is considerably much less developed than the use of catalytic Fenton to degrade organic pollutants. The main reason for the paucity of reports describing the use of Fenton chemistry to obtain organic compounds is the lack of selectivity in the product formation. Actually the high reactivity of HO• is the reason why in many cases these species can attack simultaneously to different positions of a substrate, giving rise to complex reaction mixtures in where the selectivity towards a single product is usually inadequate. Also the primary reaction products can undergo further transformation to undesirable by-products decreasing even further the selectivity at high conversions. However, on the other hand, for those substrates in where a single or preferential site for attack exists, the Fenton chemistry could be a valuable reaction to introduce hydroxyl or carbonyl functional groups. Thus, some reports have used Fenton chemistry in order to achieve valuable products such as i.e. hydroxylation of phenol to obtain hydroquinone and/or catechol or to prepare new materials by surface modification such as Fe-loaded SBA-15 through Fenton reaction [38].

The most valuable feature of the Fenton process for environment remediation is its general applicability [25,26], regardless the nature and functional groups present in the organic pollutants. Taking into account the current concerns about the quality of air and water and the negative influence for human and animal health of undesirable organic compounds, there is a renewed interest in developing general methodologies for pollution abatement, and particularly contamination caused by organic compounds [25,26]. In this regard, Fenton chemistry can contribute to recover polluted environments by effecting the transformation of organic compounds into biodegradable compounds or even direct mineralization to CO₂ depending on the depth of the Fenton process [25,26]. In this context it is worth commenting that some bioreluctant organic compounds increase significantly its biodegradability when they are submitted to Fenton reaction under *light* conditions [25,39,40]. This is due to the fact that biodegradability increases in general upon introduction of OH groups in a molecule. Therefore, a strategy that has been frequently developed in water purification consists in the combination of a Fenton treatment under mild conditions followed by biological degradation [25,39]. This strategy has the advantage of reagent economy since the chemical process does not need to produce the complete mineralization but has to effect only the transformation of a polluted medium from bioreluctant into biodegradable.

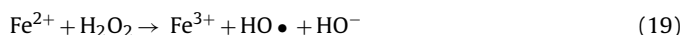
2. Advantages of catalytic Fenton processes

Considering the application of Fenton chemistry for the remediation of organic pollution one point that comes into consideration is the *benignity* of the process, this meaning that Fenton chemistry has to be limited to the minimum amount of reagents and that no environmentally unfriendly transition metals should be used. In this regard H₂O₂, easily decomposing giving H₂O and O₂ as the final products, is considered a benign reagent. However, although iron ions do not exhibit particularly negative effects for the environment, the fact that stoichiometry amounts of this transition metal are required plays an adverse effect limiting the applicability of Fenton chemistry as a general solution for pollution remediation. Also the strong acid conditions are negative from the environmen-

tal point of view since a final neutralization step can be required to obtain tolerable effluents.

The above considerations clearly point out the advantages of developing a *catalytic* Fenton process, in which HO• would be generated from H₂O₂ without the need of consuming equivalent amounts of Fe²⁺ or other transition metals. It would be even better if the catalytic Fenton process occurs at neutral or nearly neutral pH values at room temperature. Catalytic Fenton at neutral pH will consume H₂O₂ as the only reagent and will be a source of HO• without the drawbacks of iron waste and acid pH values.

One alternative to the use of stoichiometry Fe²⁺ salts has been the photo-Fenton reaction [41,42]. In the photo-Fenton reaction, upon photoexcitation hydrated Fe³⁺ undergoes a photoinduced electron transfer forming Fe²⁺ and HO• (Eqs. (17)–(19)). Eq. (18) describes the elementary photochemical step that converts hydrated Fe³⁺ into Fe²⁺ resulting in hydroxyl radical [41].



The photogenerated Fe²⁺ ion can subsequently promote a dark Fenton reaction forming Fe³⁺ and closing the cycle. The main limitation of the photo-Fenton process is the need of a transparent solution. It has to be considered that hydrated Fe³⁺ exhibits a weak absorption band in the UV region up to 400 nm ($\lambda_{\text{max}} \approx 310$ nm) and that in order to be an efficient process, most of the light should be absorbed by solvated Fe³⁺ (see Eq. (18)) [41,43]. However, most organic compounds exhibit strong absorption bands in the UV region that when present will act as internal filter impeding photon absorption by low concentrations of Fe³⁺. In common cases, polluted waters are not transparent even to the visible light, precluding the use of photochemical techniques for these samples. There are in the literature a number of reviews dealing with the photo-Fenton process and its mechanisms [44,45].

To avoid redundancy in the present review we have limited to those heterogeneously catalyzed Fenton processes that take place in the dark promoted by the presence of an inorganic solid. One obvious advantage of heterogeneous catalytic Fenton versus photo-Fenton is that the former is applicable even in those media that are not transparent to UV or visible light.

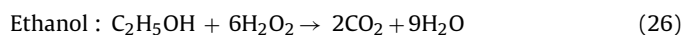
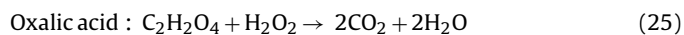
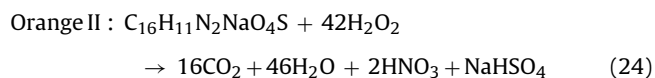
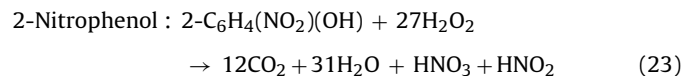
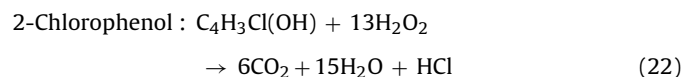
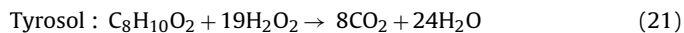
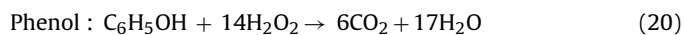
3. Scope and organization of the review

The present work summarizes those reports appeared up to late 2009 describing the use of solid catalysts based on clays, zeolites and mesoporous silicas to promote the formation of hydroxyl radicals basically from H₂O₂.

The present review, having an emphasis on the catalyst that can promote Fenton chemistry has been organized according to the nature of the catalyst support. Thus, after a few introductory, general sections describing the stoichiometry for complete mineralization, the nature of the active sites, the mechanism and main application of the Fenton Chemistry as well as the reason why catalytic Fenton processes are important, we will comment on each type of solid catalyst based on aluminosilicates to promote the Fenton reaction. Particular emphasis has been made indicating the conditions in terms of pH, temperature and H₂O₂ excess in which the catalyst have been used and the need to determine the efficiency of the catalyst from the point of view of the selectivity of H₂O₂ towards HO• generation. We will finish with general considerations about the weak points and what is still needed in this area as well as future developments on the field.

4. Hydrogen peroxide stoichiometry for complete mineralization

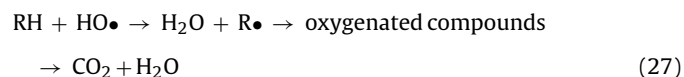
Most of the studies on catalytic Fenton reaction use a large excess of H_2O_2 . The most common reason for this excess of H_2O_2 is that according to the theoretical stoichiometry for complete mineralization many molecules of H_2O_2 are required to transform the organic compounds into CO_2 and H_2O . Eqs. (20)–(26) shows the theoretical H_2O_2 stoichiometric molar ratios based on the ideal reaction for total mineralization of some common model compounds used frequently as catalytic probes such as phenol and derivatives, Orange II, oxalic acid and ethanol [29,46–49].



Probably higher concentrations of hydrogen peroxide should be used to account for the spurious decomposition of the H_2O_2 into the hydroperoxy radicals that are considerably less reactive than hydroxyl radicals [18,50]. However, it should be noted that it has been reported that in some cases an increase of the H_2O_2 concentration has no a proportional effect on substrate or total organic carbon (TOC) degradation [51,52]. This fact is attributed to the scavenging of $\text{HO}\bullet$ by H_2O_2 (see Eq. (5)) to form the hydroperoxy radical ($\bullet\text{OOH}$), whose reactivity and oxidation potential (1.7 V) [50] is much lower than hydroxyl radical (2.8 V) and in consequence is less efficient in the oxidation process.

It is noteworthy that some authors suggest that the influence of hydrogen peroxide concentration depends on the nature of the organic compounds present in the reaction medium, the oxidation of some being hydrogen peroxide concentration independent [53,54]. This can be easily rationalized considering that if the organic compounds present in the medium are good hydrogen donors, Eq. (5) will be disfavoured or, even if formed, the hydroperoxy radical could still be reactive enough to promote similar degradation pathways as hydroxyl radicals.

One major point in Fenton-promoted, oxidative degradations is the influence of the presence of O_2 [18,27,55]. It has been established that after the initial attack of $\text{HO}\bullet$ radicals the presence of oxygen and its concentration in the medium plays an important role in the oxidative degradations that can occur through a radical chain mechanism [5–7,23,56] as indicated in Eqs. (27)–(31).



Dissolved oxygen contributes to the formation of organic peroxy radicals ($\text{ROO}\bullet$) from organic radicals ($\text{R}\bullet$) which are initially generated through hydrogen atom abstraction from R-H by $\text{HO}\bullet$ [18]. Subsequent hydrogen abstraction by $\text{ROO}\bullet$ radicals will lead to a carbon centred radical initiating again another cycle. This chain mechanism known as autooxidation only requires a substoichiometric amount of $\text{HO}\bullet$ radicals to initiate the propagating step and long propagating cycles before radical coupling. ROOH are also highly oxidizing compounds and reactive under the typical Fenton acid conditions can undergo decomposition to alcohol, ketone or even to alkoxyl radicals (Eqs. (30) and (31)) [28,57]. The last process generates two oxygen centred radicals that will trigger two new propagation chains, thus, multiplying the effect of the initial hydroxyl radical.

Since Fenton reaction is carried out in water and oxygen solubility in water is very low [58,59] (8.2 mg L^{-1} in water exposed to water-saturated air at 25°C and 1 atm.), it is frequently advisable to bubble oxygen while performing the Fenton or to keep some pressure (if possible) in the system [28,60]. Otherwise the medium can be depleted of oxygen and the degradation efficiency decreased due to the occurrence of a low turnover in the propagation steps. Accordingly, some authors have observed that the concentration of O_2 affect to the degree of substrate degradation or TOC [61]. From the above comments it appears that Fenton degradation is overlapped and reinforced by the presence of O_2 due to the occurrence of autooxidation initiated by $\text{HO}\bullet$ radicals and that sufficient attention should be paid to this issue by ensuring steady oxygen concentration or even conducting control experiments under inert atmosphere.

5. Drawbacks of Fenton reaction

Besides the large amount of Fe salts needed and the limited use of Fenton reaction in organic synthesis some other drawbacks of this reaction should be taken into account. One of them, is the pH range for application of the Fenton that is limited to a very narrow window in the range 2.5–4.0 [55]. These highly acidic solutions are generally obtained by addition of strong Brönsted acids. Although the natural reaction evolution increases the pH value up to around 5 units, it is generally necessary a final neutralization step. In addition, it is necessary to implement the Fenton treatment with additional separation steps in order to separate the iron sludges from the treated water after the reaction and neutralization step. For example, one promising application for Fenton chemistry is a pre-oxidation step prior to a biological degradation process when a high percentage of bioreluctant organic compounds (i.e. aromatic moieties) can produce bacteria inhibition [62]. A second general application is the treatment of a large number of heavily polluted aqueous effluents from industrial sources (i.e. effluents of oil fields and transportation, petrochemical industries, kraft and paper milling, olive oil production, textile industries and various chemical plants) with a wide type of pollutants (phenolic and derivatives, chlorophenols, herbicides, pesticides, solvents, paints, polymers and others) that also require an appropriate separation and management of the iron sludges [46].

To solve or minimize these problems caused by the presence of iron ions in the effluents and reduce the recovery cost, the use of heterogeneous Fenton-like catalyst is a promising alternative that could allow also operation under conventional continuous flow reactors without the need of soluble iron salts and hopefully at neutral pH and ambient temperature.

6. General features for efficient Fenton catalyst

Considering the wide range of substrates that can be selected as model compounds and the range of reaction conditions it is convenient to describe in this section what would be the most important parameters that should be determined in order to rank different materials according to their activity to promote the Fenton reaction.

The first important parameter is catalytic activity and stability of the material. In general, reusability in several runs is not a good criterion for stability of the catalyst since reusability depends on the substrate-to-catalyst ratio. Thus, in general, using large excesses of solid should be always possible to reuse the material in several consecutive reaction runs. Lesser amounts of solid catalyst would make reusability more difficult. Considering the large variability in the amount of catalyst used it is better to provide data of the maximum productivity. This can be measured by performing a particular test in which a large excess of substrate is used and the reaction is prolonged until complete deactivation of the catalyst. At this time, besides obtaining data on the maximum productivity the catalyst must be deactivated and it would be pertinent to determine the main cause of deactivation and to devise simple reactivation protocols. In the case of the Fenton reaction using phenol as substrate, carboxylic acids are common reaction by-products and they can act as poison of metal ions by forming metal complexes. In these cases washing under basic pH could be a valid reactivation procedure provided that the metal ions or active sites can stand these washings.

Related to the stability of the solid catalysts and their use as heterogeneous catalysts, absence of leaching of metal species from the solid to the aqueous phase is one key issue since this process can afford a minimum concentration of the metal species in solution that can act as homogeneous catalyst. Therefore, in those cases in where leaching occurs the overall catalytic activity could be a combination of the activity of the leached species plus the activity of the solid catalyst, and it is necessary to determine the contribution of both processes to the experimental activity. One disadvantage of leaching is that it produces depletion of the metal sites in the solid and, at long term, this will cause the loss of solid catalytic activity.

Since Fenton requires the use of H_2O_2 , besides monitoring the disappearance of mineralization of the organic substrate, the perfect Fenton catalyst should also be selective in the use of H_2O_2 . Therefore, it is always necessary to evaluate the material for the decomposition of H_2O_2 . Moreover, generation of free hydroxyl radicals in the presence of the solid catalyst must always be addressed by determining the characteristic products formed by $\text{HO}\cdot$ attack and by performing quenching experiments with alcohols or some other quencher that should stop the Fenton degradation. In the ideal case, the consumption of H_2O_2 and phenol should be stoichiometrically related indicating that the consumption of H_2O_2 in spurious processes has been minimized.

As we have commented earlier, homogeneous Fenton chemistry is very sensitive to the pH and cannot occur for pH values higher than 4. This is due to the formation of metal hydroxides that can be insoluble and undergo phase separation. In the case of solid catalyst for Fenton chemistry, tests have to be performed to assess the influence of the pH on the catalytic activity. As a general rule, the target is to develop efficient solid catalysts for Fenton reaction at neutral or near neutral pH and room temperature.

Other parameters that have to be considered include sufficient description of the preparation procedure and firm characterization data in order to ensure reproducibility of the material and the catalytic performance. This point is particularly relevant considering that very frequently speciation of the aquated metal ions is very sensitive to the pH of the solution and that formation of metal oxides can take place at least in part during the preparation of the material. In this way, even if the same supports are used, it could be

that very different catalytic activity is obtained simply because iron speciation is very sensitive to pH, aging and nature of the support and this leads to different active sites.

From the above comments it is clear that in order to properly study the catalytic activity of some materials not only the disappearance of the substrate but also the products formed, the decomposition of H_2O_2 , the absence of leaching and the experimental conditions range in which the solid exhibits catalytic activity have to be evaluated. It is also advisable that the study includes mechanistic details confirming the intermediates of hydroxyl radicals and providing the main deactivation path of the solid.

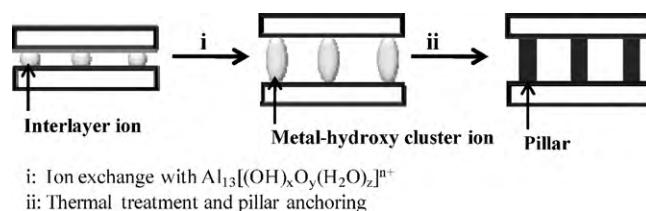
After these introductory sections, a detailed description of the use of clays, hydrotalcites, zeolites and silicas as solid catalysts for the Fenton reaction will be presented and constitutes the main body of this review.

7. Clays

Clays are natural abundant minerals that can be obtained from some mines in high purity. Most of the works describing clays for Fenton catalysis are using these natural samples from various origins (montmorillonites from Wyoming, Texas, Spain, France, Saponite from Iberian Peninsula etc. directly or after purification). Considering the high purity of these natural montmorillonites, there is not much need in using synthetic samples prepared in the laboratory. Nevertheless, there are a few examples in where iron containing synthetic clays have been tested as solid catalyst to promote the Fenton reaction [63]. Layered clays is one type of clay in where the structure of the aluminosilicate defines sheets having an excess of negative charge that interact strongly by electrostatic forces with charge balancing cations, typically alkali metal ions, located in the intergallery space [64–67].

In spite that layered clays are constituted by sheets with a large total surface area the interlamellar space is generally not accessible to any substrate due to the strong electrostatic interaction between sheets and charge balancing cations. Thus, there has been a large interest in making accessible the interlamellar space of layered clays. This can be made possible by putting large cations (“pillars”) between the sheets. Scheme 2 illustrates the structural changes and the increase in the porosity and surface area as consequence of the ion exchange/calcination with polyaluminium cations.

The use of pillared clays (PILC) as Fenton catalyst has been frequently reported [68–70] and indeed this type of solids is one of the favourite materials to promote Fenton decomposition of organic compounds. They combine the availability and robustness inherent to clays to the large surface area and catalytic activity imparted by the pillars. The pillars are generally polycationic species of large size that being located in the interlamellar spaces increase the distance between the clay sheets and make accessible the intergallery space to molecules [71]. This increase in surface area generally plays a positive role making accessible the catalytic sites. In addition, the pillars made by a combination of Al with other metals (i.e. iron) introduces additional catalytic sites [72] or they constitute the actual catalytic sites. While as commented before the crystal structure of layered clays is relatively well defined, the structure



Scheme 2. General process of pillaring clays.

of the pillars that frequently are responsible for most of the catalytic activity is considerably much poorly defined. Pillars are very often polycationic oxo-hydroxy species of one or various metals. In addition, it can be anticipated that considering the large number of variables in the preparation of the pillars [71,73] such as pH, concentration of metal ions, temperature, aging etc. changes in the experimental protocol can lead to variations in the composition and structure of the pillars. Therefore it can be anticipated that differences in the catalytic activity can derive from differences in the preparation procedure and composition of the pillars. The difficulty in having pillars constituted by a single species or with a homogeneous distribution of polycations [74] also casts doubts about the reproducibility in the preparation of this type of catalyst and the reliability of the catalytic tests, particularly because the decomposition of H_2O_2 is very sensitive to metal impurities.

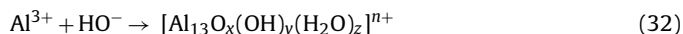
7.1. Montmorillonites

Montmorillonites are natural layered clays whose structure is formed by AlO_6 octahedra sandwiched by SiO_4 tetrahedra [66]. The presence of Al in the framework introduces negative charges that require the presence of charge balancing cations occupying interlamellar spaces. Typically the charge compensating cations are K^+ , Na^+ or alkali earth metals. Occasionally some Fe, Mg, Mn or other transition metal can isomorphically replace framework aluminium in a small degree and this can be revealed by elemental analysis. Ion exchanged montmorillonites have been widely used as solid catalysts to promote Brønsted and Lewis acid reactions as well as redox transformations [75–80].

Partial substitution of small cations by large cations produces the separation of the layers, increasing the layer interdistance, and creating porosity in the material [80]. Among the preferred large cations, those polyaluminium cations have been the most widely used [80–83]. One advantage of polyaluminium cations is that no foreign metal different from aluminium and silicon already present in the montmorillonite are introduced. Moreover, considering that the nature of the polyaluminium cation is not that different from the coordination sphere of aluminium in the layers, thermal treatment of the montmorillonite with expanded interlayer distance produces the formation of covalent bonds (“grafting”), between the layer and the bulky cation in the interlamellar space (see Scheme 2). These covalent bonds between the layers and the polyaluminium cation determine that no further ion exchange of these large cations can occur and originates additional strength in the material towards calcination, steaming, abrasion, etc. This covalent linkage between the large cation and the layers is described commonly by “pillaring”, the resulting clay being denoted as pillared clay.

As commented before the most widely used pillar to prepare expanded clays is an ill-defined mixture of polyaluminium cations in which predominates a polyelectrolyte with 13 aluminium atoms connected by oxo and hydroxy bridges that is obtained by hydrolysis and condensation of Al^{3+} salts at controlled basic pH, i.e. Johansson's ε -Keggin $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ polycation is obtained from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (10 ml, 5 mmol) aqueous solution, by addition of NaOH (1 M, 12.3 ml) at a molar ratio $h = n_{\text{OH}}/n_{\text{Al}} = 2.46$, at 90°C , with strong stirring [84]. Eq. (32) indicates the formation

of Al_{13} polycation from Al^{3+} salt. These pillared clays have also been widely used in heterogeneous catalysis as an improved generation of clay derived materials [83,85]. Typically the presence of pillars renders accessible the internal surface of the layered clay and introduces open microporosity in the otherwise non-porous clay. Accessibility of non-cationic substrates to the intergallery space of pillared clays increases considerably the catalytic activity of pillared clays with respect to the original montmorillonite.



In view of the wide use of pillared montmorillonites as heterogeneous catalyst, it is not surprising the series of reports describing the catalytic activity of pillared clays for the Fenton reaction. Some of these reports specifically deal with the preparation of pillars containing other metals besides aluminium.

Besides Fe^{2+} , Cu^{2+} is other transition metal ion that has general catalytic activity for Fenton reactions. The influence of the experimental procedure for Cu^{2+} doping on Al-pillared clays on the activity for the wet peroxidation of model pollutants tyrosol has been studied [48]. Starting from a natural montmorillonite, pillaring with polyhydroxyoxaluminium was carried out following the conventional procedure consisting on the treatment of a diluted montmorillonite suspension with a solution of aluminium nitrate using an OH/Al molar ratio of 2.25. The pH of the resultant pillared solution was 3.8. After the preparation of the Al-pillared clays copper was finally introduced in the solid state (“solid ion exchange”) by mixing intimately $\text{Cu}(\text{NO}_3)_2$ and the Al pillared clay in a mortar. The resulting Cu^{2+} containing Al-pillared clay was finally submitted to calcination at 300°C for 3 h under controlled atmosphere. For one sample, helium was flushed through the solid during the calcination, while in another sample an oxygen flow was passed through the system. While both, He and O_2 purged, Cu^{2+} -containing Al-pillared clays have the same copper loading, the calcination procedure influences dramatically gas adsorption and surface area of the resulting copper clay. It was found that calcination under helium is more convenient than under oxygen to obtain higher surface area and pore volume [48]. The reasons for this result appear to be related to the particle size and copper distribution through the solid, helium flow rendering a material with smaller and more uniformly-distributed copper particles than treatment under oxygen atmosphere. Table 1 summarizes the main textural analytical properties of the samples.

Working with this copper containing Al pillared clays as solid catalyst, the decomposition of tyrosol by H_2O_2 has been studied [48]. Tyrosol is a natural compound present in olive oil mill waste waters [86]. In Mediterranean countries that produce large quantities of olive oil notoriously bioreluctant waste waters with high phenol content are formed [87,88]. Up to now, there is not a suitable physical or biological treatment to remediate the pollution caused by this olive oil waste water [87]. Fenton chemistry could be a suitable procedure that could reduce the carbon content and chemical oxygen demand of this type of waste water [89,90]. In this context tyrosol (see structure in Fig. 1) present in significant percentage in olive oil mill waste waters can be considered a good model compound for the complex mixture present in olive oil mill wash out.

Table 1
Textural properties of fresh and used Cu^{2+} -containing Al-pillared montmorillonites calcined at 300°C under He or under O_2 derived from the nitrogen adsorption/desorption isotherms at 77 K. Data taken from ref [48].

Catalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{ext} ($\text{m}^2 \text{g}^{-1}$)	S_{int} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$)	$V_{\mu p}$ ($\text{cm}^3 \text{g}^{-1}$)	Cu (wt%)
Al-PILC	204	67	137	0.120	0.080	0
CuN_{He} -PILC	123	23	100	0.115	0.048	1.93
CuN_{O_2} -PILC	52	32	20	0.065	0.029	1.93
Used CuN_{He} -PILC	27	19	8	0.061	0.019	
Used CuN_{O_2} -PILC	12	7	5	0.035	0.002	

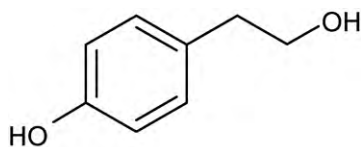


Fig. 1. Chemical structure of Tyrosol.

Preliminary studies [48] on the influence of catalyst concentration, amount of H_2O_2 , and reaction temperature has established that optimal conditions to treat 500 mg L^{-1} of tyrosol can be 500 mg L^{-1} of catalyst, stoichiometric amount of H_2O_2 for its complete mineralization (19 equivalents with respect to tyrosol, see equation 21) and temperatures above the ambient. In this way, tyrosol conversions higher than 96% are reached at 1 h at 40°C and 6 h at 25°C . TOC removals around 60% can be obtained using the helium treated Cu^{2+} -containing Al-pillared clay at 24°C in 24 h. Oxalic acid has been characterized as the major degradation product, representing more than 98% of the TOC for the reaction beyond 24 h. This data suggests that Cu^{2+} -containing pillared clay is more efficient than analogous Fe^{3+} -containing pillared clay for the total mineralization of tyrosol according to the authors [48]. The Cu^{2+} -containing pillared clay catalyst was reused in two consecutive runs after filtration, exhaustive washings with water and drying at 100°C . While it was observed that the Cu^{2+} -containing pillared clay prepared by calcination of the $\text{Cu}(\text{NO}_3)_2$ Al-pillared clay mixture in the presence of oxygen becomes completely deactivated after the third run, the analogous material in which calcination was carried out under helium undergoes a gradual decrease in activity of about 20% in the third use. Moreover, although copper was detected in the aqueous phase after the use of the material as catalyst, the leaching in a single run was 0.8% of the total copper content in the solid and consequently the contribution of this dissolved copper to the overall activity was considered negligible [48].

The material obtained by helium calcination was also tested in a continuous flow reactor at 60°C . Fig. 2 shows the plot of tyrosol and TOC concentrations over the time for a continuous flow (30 mL h^{-1}) experiment having 3.5 mM tyrosol and 66.5 mM H_2O_2 (stoichiometric amount to achieve theoretical mineralization) concentrations in the feed and initial pH 5.6. In this figure the two first points at shortest time correspond to the value of tyrosol disappear-

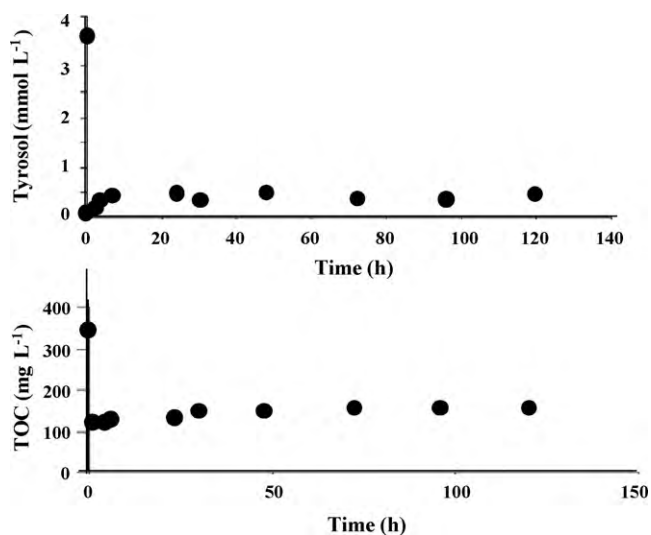


Fig. 2. Plot of tyrosol and TOC concentration against time for Cu^{2+} -containing Al-pillared clay treated under He using a continuous reactor. Reaction conditions: 1 g catalyst; flow rate 30 mL h^{-1} ; temperature: 60°C ; 3.5 mM tyrosol; 66.5 mM H_2O_2 (figure taken from ref. [48]).

ance and TOC decrease in the feed and at the exit of the reaction. It has observed that before reaching the stationary regime of operation the percentage of tyrosol decrease is larger probably due to the overlapping of degradation and adsorption at short time on stream. The data presented in Fig. 2 are remarkable and indicate a high stability of the catalyst during the reaction for long times on stream [48]. Oxalic acid was also the main product detected in the continuous flow experiments.

The difference in activity of the copper-containing Al-pillared clay depending on the calcination atmosphere was attempted to be rationalized by temperature-programmed reduction (TPR) study [48]. For both samples hydrogen gas uptake suggests the presence of several copper oxide species in different proportions. One of these species has been attributed to copper oxide anchored to the aluminium pillars. The higher activity and stability of the material obtained by calcination under He was attributed to a better link of the Cu^{2+} to the Al polyelectrolyte pillars of the clays, which renders these Cu^{2+} ions more stable and decreases their tendency to leach and interact with the oxalic acid present in the solution. In the case of the used catalyst the disappearance of some copper species was observed by TPR and a simultaneous IR study has shown the inclusion of some oxalate in the material probably forming copper oxalate. However, evidence for this proposal based on TPR is weak compared to chemical analysis and the reason why calcination under oxygen is unfavourable with respect to helium requires further study in order to produce a material in which the population of optimum copper sites is maximized. It could be that copper oxides formed in the calcination under oxygen are formed on less extent when the calcination is carried out under helium.

7.2. Bentonites

Among the reported pillared clays as oxidation catalysts, Tati-bouët and co-workers [61] have described the use of a bimetallic pillared bentonite for the degradation of phenol by H_2O_2 . In this example the pillars were obtained by co-hydrolysis of $\text{AlCl}_3/\text{FeCl}_3$ in 0.2 M NaOH. The resulting pillared clay has a d_{001} spacing of $1.84 \pm 0.02 \text{ nm}$ that corresponds to an interlayer space of about 0.8 nm . The surface area and pore volume determined by nitrogen absorption were estimated as $240 \text{ m}^2 \text{ g}^{-1}$ and $0.14 \text{ cm}^3 \text{ g}^{-1}$, respectively. Supposedly, the presence of iron in the pillar renders the resulting pillared clay active for the peroxide oxidation. However, considering that natural clays already contain some iron in their composition, control tests in which the original bentonite and bentonite having only aluminium pillars are used as blanks should have been presented to firmly support the need of Fe^{3+} in the pillars to observe catalytic activity in the clay.

Preliminary experiments in homogeneous phase using soluble iron salt (2 mg L^{-1}) and 16.8 equivalents of H_2O_2 at room temperature reveal that phenol decomposition and TOC abatement were remarkably dependent on the pH of the solution in the range 2–6.5 and on the presence or absence of oxygen [61]. No indication of how the pHs has been controlled or if the pH values referred exclusively to the initial value rather than to a fixed value were given. Both parameters, phenol decomposition and TOC decrease, follow the same profile. Importantly, it was found that the presence of oxygen increases significantly both parameters. This has been interpreted as indicating that propagation steps involving radicals generated upon the initial attack of hydroxyl radicals to phenol increase in the presence of oxygen by oxygen trapping of the radicals. Using a phenol solution (100 mL , 0.5 mM initial phenol concentration) and continuous H_2O_2 addition (0.1 M at a flow of 2 mL h^{-1}) at 70°C and pH 3.5 and 10 g L^{-1} of Al/Fe-pillared bentonite about 80% of phenol was transformed into CO_2 in 2 h [61]. These values correspond to 8 mmol of H_2O_2 per mmol of phenol that represents around one half of the theoretical value of H_2O_2 for mineralization of phenol

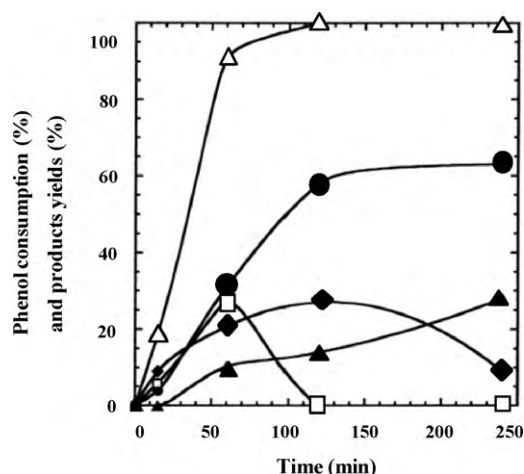


Fig. 3. Product distribution as a function of time for the H_2O_2 degradation of phenol in the presence of Al/Fe-bentonite catalyst ([catalyst] = 5 g L^{-1} , $T = 25^\circ\text{C}$). Δ : phenol conversion (%); \bullet : TOC abatement (%); \square : catechol + hydroquinone; \blacklozenge : other intermediates; \blacktriangle : oxalic acid (figure taken from ref. [61]).

(see Eq. (20)). Under other conditions lower TOC reductions are obtained. As an example Fig. 3 shows the temporal evolution of phenol consumption, product yields and TOC decrease when phenol degradation by H_2O_2 in the presence of Al/Fe-pillared bentonite is carried out at room temperature.

It is interesting to note in this plot that the total concentration of phenol, catechol and hydroquinone and the TOC decrease follow parallel profiles and once phenol, catechol and hydroquinone have disappeared, no further TOC reduction is observed [61]. At this point oxalic acid is present in significant concentrations. Apparently oxalic acid is very stable to degradation under these reaction conditions and accumulates at long reaction times without being transformed into CO_2 .

The Al/Fe-pillared bentonite was found to act as heterogeneous Fenton catalyst, since the concentration of iron leached from the solid to the aqueous phase was below 0.35 mg L^{-1} and negligible from the catalytic point of view. Interestingly, Al/Fe-pillared bentonite was more active than iron species in homogeneous phase. The material could be reused three times giving upon reuse even higher activity than the fresh material [61]. No explanations for this increase in catalytic activity upon use were given.

Using an Al/Cu-pillared bentonite Barrault et al. [91] have shown that the preparation procedure can influence the catalytic activity of the material for phenol degradation by H_2O_2 . In classical pillaring procedures two aqueous solutions one of them containing the suspended clay and the other the pillaring solution are mixed. It was considered that this conventional procedure is disadvantageous due to the handling large water volumes (two solutions). These authors consider more convenient to use a modified method in which dry clay powder is directly dispersed in the pillaring solution [91]. The pillar solution was obtained from a mixture of $\text{Al}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ to which NaOH was added to bring the pH at

around 3.8. Above this pH, the Cu^{2+} ions hydrolyze and precipitate as hydroxide. The preparation procedure determines that the Cu^{2+} content and surface area of the resulting solids varies and therefore it can be assumed that these variations will be reflected also in the catalytic activity. In fact it was determined that the procedure adding dry bentonite clay to the pillaring solution renders a material with the highest Cu^{2+} content, surface area and catalytic activity for Fenton degradation. Leaching of Cu^{2+} from the solid to the solution was found to contribute in a negligible amount to the degradation of phenol. In addition the Al/Cu-pillared clays can be reused five times without observing any change in the reaction rate. A study on the difference in behaviour between using dry clay or mixing two suspensions in the preparation of the catalyst shows, however, that the differences in catalytic activity become less relevant when higher amount of hydroxide is added. In any case it is clear that the most convenient and simplest experimental procedure of adding dry clay powder to the pillaring solution renders catalytically active clays without the need of suspending and swallow previously the clay in an aqueous solution. Concerning the influence of the presence of Cu ions in the pillars the authors comment blank control experiments for phenol oxidation using a pillared clay with pure aluminium oxyhydroxides pillars in where very low activity was observed. However the data were not presented in numerical or graphical form.

Carriazo et al. reported a study about pillaring natural Colombian bentonite [92] showing that the presence of cerium in the pillar renders the resulting material more active for phenol degradation than the parent one in which the pillars contain aluminium and iron. This positive effect of the Ce incorporation has been attributed in part to the increase in the basal space and surface area when Ce atoms are present in the pillars.

The catalytic activity of these pillared clays (5 g L^{-1}) was tested for the phenol oxidation (0.5 mM) under continuous addition of H_2O_2 (0.1 M at a constant flow of 2 mL h^{-1} during 4 h) at room temperature and pH 3.7 under aerated solution [92]. This H_2O_2 dose at 4 h represents around the theoretical stoichiometric amount for phenol mineralization (see Eq. (20)). The results in Table 2 show that aluminium pillared clays already exhibit a remarkable catalytic activity due to the iron content of the natural clay and the surface increase by pillaring. When the pillar contains Al and Ce the catalytic activity increases even further and only increases marginally when ternary Al, Ce, Fe pillars are used.

These results illustrate the beneficial influence of pillaring and particularly pillaring with Ce in the catalytic activity of clays. However as it can be seen in the Table 2 similar results can be obtained just using binary Al, Fe pillars and, thus, the benefits of Ce versus Fe are not evident [92].

One of the major drawbacks of pillared clays is the ill-defined nature of the species forming the pillars. This complicates considerably characterization and, furthermore, compromises reproducibility of the catalytic activity. Thus, an analogous study [74] on the nature of the species forming the pillars of Al and Al-Ce-Fe pillared bentonites used as catalysts for the Fenton reaction has led to the conclusion that the pillars are constituted by inde-

Table 2
Phenol and TOC conversions at 25°C , atmospheric pressure and pH 3.7 after 4 h of reaction [92].

Solid	Conversion of phenol (%)	Conversion of TOC (%)	Metallic leaching (mg L^{-1} Fe in solution)
Al-Fe-PILC (8.75 wt.% Fe; 11.72 wt.% Al)	100	50	0.21
Al-Ce-Fe-PILC (8.68 wt.% Fe; 11.83 wt.% Al; 0.1 wt.% Ce)	100 ^a	54	0.25
Al-Ce-Fe-PILC (7.34 wt.% Fe; 11.99 wt.% Al; 0.13 wt.% Ce)	100 ^a	52	0.34
Al-Ce-Fe-PILC (6.16 wt.% Fe; 12.28 wt.% Al; 0.13 wt.% Ce)	100	55	0.27
Al-Ce-PILC (6.06 wt.% Fe; 12.38 wt.% Al; 0.14 wt.% Ce)	100	51	0.21
Al-PILC (6.06 wt.% Fe; 12.48 wt.% Al)	100	39	0.20
Natural clay (calcined) (6.03 wt.% Fe; 9.83 wt.% Al)	48	5	0.30

^a Reached during the first hour of reaction.

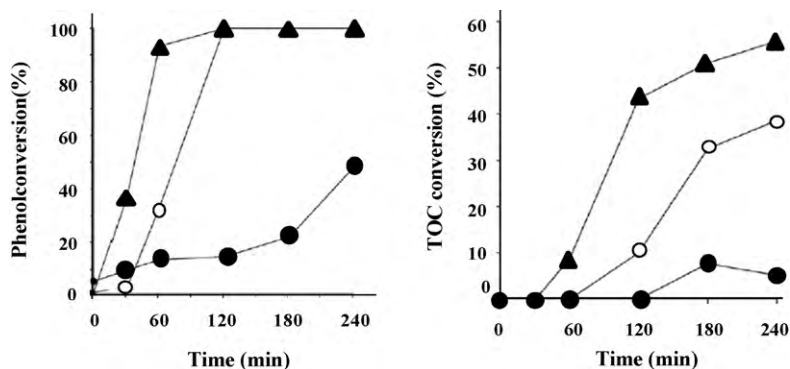


Fig. 4. Catalytic activity of natural clay (calcined at 400 °C) and pillared clay. ▲AlCe(10)Fe(10)-bentonite; ○ Al-bentonite; ● Bentonite (figure taken from ref. [74]).

pendent phases of aluminium oxide (boemite), cerium oxide and iron oxide (hematite). Probably the hematite has some small level of isomorphic substitution of Fe^{3+} by Ce^{4+} as suggested by the shifts in the X-ray diffractogram (XRD) of the corresponding hematite peaks of the pillars. Thus, even if the mother solution used for the pillar preparation contains simultaneously several metal ions it happens that, when forming the polyhydroxy metal clusters, the metal ions segregate in independent phases rather than a single mixed double or triple metal oxide phase containing simultaneously all the metal ions. In the case of the study commented [74], the initial solution contains nitrate salts in appropriate proportions of the three metals (80:10:10 for Al, Ce and Fe, respectively) when NaOH is added until the HO^- to total metal ion ratio is about 2 and the pH increase produces the formation of the pillar phase, segregation of each metal in a different phase occurs.

If this is the case, it seems also reasonable to assume that solid phase synthesis in which the components of the pillars and a pillared clay are simply mixed and backed should not be an efficient process to effect the incorporation of the new metal into the pre-formed pillars [74] as previously proposed for Cu on Al-pillared montmorillonite [48]. In any case, the study on multimetallic pillared clays has shown that even though the pillars are constituted by three independent phases, the resulting material exhibits a significantly improved catalytic activity, both for the phenol disappearance and for the decrease on TOC, with respect to samples of pillared clays lacking the metal cocktail [74]. Fig. 4 presents a comparison of the activity for phenol degradation and TOC reduction using H_2O_2 as oxidizing reagent and the not pillared, the Al-pillared and the Al-Ce-Fe-pillared clays. The induction period observed in the TOC decrease corresponds to the time needed for the consecutive cascade reactions going from phenol to carbon dioxide, therefore showing a dephasing with respect to phenol degradation. These results show that the major factor influencing the catalytic activity is the increase in the surface area and porosity in the original clay by pillaring, and that the nature of the pillar plays a secondary role. Another important outcome of this study [74] is that it is not necessary to claim that the pillar is constituted by a single phase to observe an improved catalytic performance in this type of material. However it would had been interesting to compare the catalytic activity of the pillared clays with an analogous Al,Fe pillared clay to clearly reveal the influence of Ce on the Fenton activity of the materials.

7.3. Saponite

Another example of a natural layered clay that has been Al-pillared and used as heterogeneous Fenton catalyst is saponite [29]. In this case, Fe ions were introduced at several loadings from 7.5 to

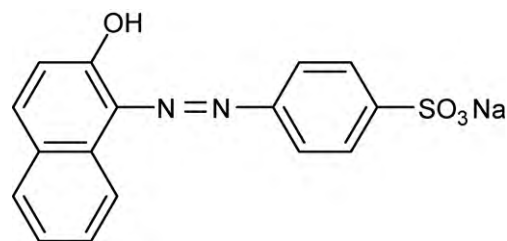


Fig. 5. Chemical structure of Orange II.

17 wt.% weight using different precursors including Fe(II) oxalate, Fe(II) and Fe(III) acetylacetonate and Fe(II) acetate. Since the preparation procedure includes a calcination step, the leading idea was to determine if the nature of the precursor influences the final iron species remaining on the clay. These clays were tested for the decomposition of Orange II (see structure in Fig. 5) considered as a model pollutant for other dyes used in the textile and pulp and paper industries. The catalytic tests were performed using 97 mg L^{-1} of the solid that is an amount much lower than those commonly employed for similar clay-based catalysts that typically are around 1 g L^{-1} . No clear influence about the influence of the nature of the iron precursor on the catalytic activity of the resulting pillared clay was obtained, although Fe(II) oxalate at the highest loading (17 wt.% Fe^{2+}) is proposed as a convenient precursor for this application [29].

As generally observed for the Fenton reaction the pH, temperature and concentration of H_2O_2 play a role on the resulting activity. No dye degradation was observed at pH values of 4 or higher and most of the study was carried out at pH 3 [29]. Typical experiments were performed using 60 equivalents of H_2O_2 and it was found that larger excesses of H_2O_2 are unfavourable because the $\text{HO}\cdot$ reacts with H_2O_2 according Eq. (5) rendering less reactive hydroperoxyl radicals ($\text{HOO}\cdot$). The solid catalyst was reused four times, observing a moderate decrease in the catalytic activity upon reuse, probably due to the occurrence of iron leaching.

Concerning the influence of the reaction temperature, it was observed that in the range from 10 to 70 °C there is an abrupt increase in efficiency from 10 to 30 °C, and above this temperature only minor activity enhancement was observed up to 70 °C [29]. This observation seems to imply that the initial reaction rate does not obey the Arrhenius law, although no reason for this were given.

7.4. Synthetic clays

Natural clays are widely abundant minerals that can be mined with high purity. However, even though natural clays can be obtained with reasonable purity from the structural point of view,

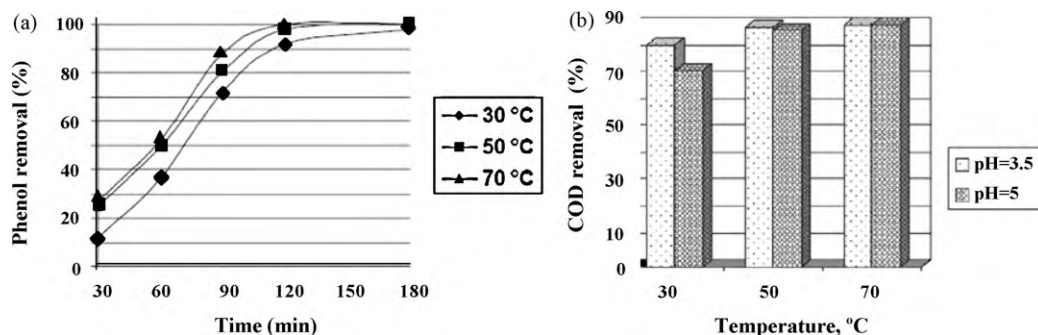


Fig. 6. (a) The influence of temperature on phenol removal efficiency at pH 5.0; 2.66 mM phenol, 50 °C, 0.5 g L⁻¹ PILC catalyst, 37.23 mM H₂O₂. (b) The effect of the temperature on COD removal at various pH values, 2.66 mM phenol, 0.5 g L⁻¹ PILC catalyst, 37.23 mM H₂O₂ (figure taken from ref. [63]).

they always contain minor percentages of isomorphous substitution of Al by other metal ions occupying octahedral positions. Among them, Fe is one of the elements that are present in minor amounts. It has been speculated that the presence of this Fe, as well as other transition metal ions such as Mn, Cr or V, can introduce catalytic activity.

In order to address this issue, one possibility is to use synthetic clays prepared with purer transition metal precursors. However, in contrast to zeolites, clays are difficult to be prepared in the laboratory and there are only a few and scattered works on synthetic clays.

One of these examples has used beidellite obtained by hydrothermal synthesis using hydrofluoro acid as medium [63]. This synthetic clay, after pillaring with aluminium, was treated with NaCl aqueous solution (1 M) at various pHs (NaOH as base to set the pH value) and 60 °C for long times to introduce exchangeable positions in the material. After treatment with NaCl, the Al-pillared beidellite could be further ion exchanged with iron nitrate to introduce iron in the material. It was found that the final iron loading depends quasi linearly on the pH of the hydrothermal treatment with NaCl up to pH 9 in where a plateau is reached and no higher iron loadings were achieved.

This synthetic iron-exchanged Al-pillared beidellite was used as heterogeneous catalyst for the Fenton degradation of phenol in aqueous phase [63]. Several parameters affecting the catalytic activity were studied. It was found that Fe-exchanged, Al-pillared beidellite was active at 50 °C even at neutral pH, although its activity increases as the initial pH value of the solution decreases. However, since the reaction was carried out without pH buffering, it was observed that as the reaction proceeds the initial pH value drops and this leads to a process acceleration. As a side effect of the pH drop, leaching of iron ions from the solid to the solution also increases. However, it was found that the activity of the leached iron is negligible and all the catalytic activity is related to the presence of the solid synthetic clay. The fact that the synthetic clay catalyst is active at pH values higher than pH 4, the limit pH value in homogeneous Fenton above which there is no reaction, was interpreted as indicating that the clay is acting stabilizing on its surface some iron species that are still catalytically active even though the solution pH is higher than 4.

Concerning the reaction temperature it was found [63] that the efficiency of phenol disappearance and chemical oxygen demand (COD) removal increases with the temperature up to 50 °C and above this value further improvements were negligible. As it can be seen in Fig. 6 even the initial reaction rate obtained from the time-conversion plot seems to be independent of the reaction temperature, a fact that deserves further study.

Similarly the amount of catalyst present in the system exerts a strong influence on COD removal up to 0.2 g L⁻¹ and above this value up to 1 g L⁻¹ the differences are less important. This catalyst

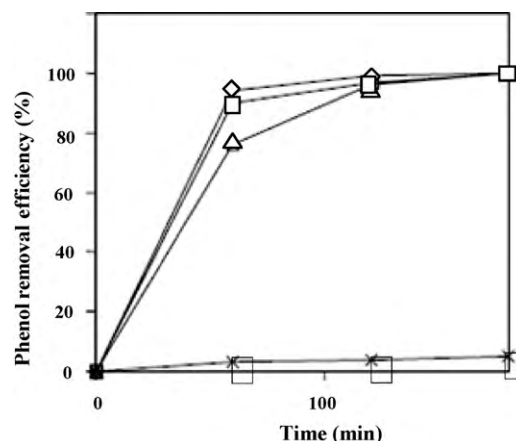


Fig. 7. Conversion of phenol as function of reaction time in the presence or absence of Fe-exchanged Al-pillared synthetic beidellite: (a) fresh catalyst (◇ 1st run); (b) reused once (□ 2nd run); (c) reused twice (△ 3rd run); (d) after filtration of the catalyst (× filtered solution) and the addition of phenol and H₂O₂. Reaction conditions: 0.5 g L⁻¹ beidellite, 2.77 mM phenol, 37.23 mM H₂O₂, initial pH 3.5, 50 °C (figure taken from ref. [63]).

was tested in three consecutive reuses (see Fig. 7) with no significant differences in the final percentage of phenol removal but with some clear and consistent decrease on the reaction rate suggesting that further reuses cannot be guaranteed.

The following Table 3 compiles some other results that have been reported using clays and pillared clays as heterogeneous catalysts for the Fenton reaction for the degradation of phenol and decoloration of Orange II, as well as for phenol hydroxylation [54,55,72,74,93–100]. This Table indicates the composition of the pillar and the best reaction conditions tested.

8. Hydrotalcites (anionic clays)

Hydrotalcites are layered double hydroxide-oxides (LDH) with MgO brucite-like structure containing two different metals one of them dipositive and the other tripositive [64,71]. The presence of a metal with +3 oxidation state introduces a net positive charge in the layer that requires the presence of equivalent amounts of anions occupying the intergallery space. One of the most widely employed hydrotalcite is the one having Mg and Al (Mg/Al atomic ratio 3:1) in the layers and having carbonate as a compensating anion [101].

Hydrotalcites can be easily obtained in the laboratory by mixing an aqueous solution containing soluble salts of the two cations in the appropriate proportion with a basic aqueous solution containing the corresponding anion that will occupy the interlamellar space [64,71,102,103]. Fig. 8 shows the crystal structure common to hydrotalcites.

Table 3

Summary of the results reported for Fenton reaction using clays and pillared clays as heterogeneous catalysts.

Catalyst	Catalytic activity		Reaction conditions	Ref.
	Substrate conversion (%)	TOC decrease (%)		
Montmorillonite clay				
Fe,Al-PILC (1.5 wt.% Fe)	100	40	Catalyst 1 g L ⁻¹ , 1 mM phenol, 14 mM H ₂ O ₂ , pH 6.2, 50 °C, 1.5 h reaction time	[93]
Fe,Al-PILC (1.5 wt.% Fe)	100	nd ^a	Catalyst 2 g L ⁻¹ , 0.1 mM monoazo dye acid chrome dark-blue, 6 mM H ₂ O ₂ , pH 5.8, 40 °C, 5 h reaction time	
Fe,Al-PILC (8.1 wt.% Fe)	90	nd	Catalyst 1 g L ⁻¹ , 1 mM 4-nitrophenol, 10 mM H ₂ O ₂ , 5 h reaction time	[94]
Cu,Al-PILC (0.2 wt.% Fe, 0.7 wt.% Cu, 14.0 wt.% Al)	nd	30	Catalyst 1 g L ⁻¹ , 1 mM phenol, 14 mM H ₂ O ₂ , pH ₀ 6.2, 50 °C, 4 h reaction time	[95]
Fe,Cu,Al-PILC (1.0 wt.% Fe, 0.05 wt.% Cu, 12.8 wt.% Al)	nd	39		
Fe,Cu,Al-PILC (1.3 wt.% Fe, 0.06 wt.% Cu, 10.9 wt.% Al)	nd	40		
Fe,Cu,Al-PILC (1.5 wt.% Fe, 0.06 wt.% Cu, 10.9 wt.% Al)	nd	52		
Fe,Al-PILC (1.7 wt.% Fe, <0.01 wt.% Cu, 13.8 wt.% Al)	nd	48		
Fe,Cu,Al-PILC (1.8 wt.% Fe, 0.17 wt.% Cu, 12.8 wt.% Al)	nd	–		
Al-PILC.bnt ^b (12.3 wt.% Al)	15 ^d	nd	Catalyst 5 g L ⁻¹ , 100 mL phenol (0.5 mM), 2 mL h ⁻¹ H ₂ O ₂ (0.1 M) (12 equiv respect phenol), pH 3.5–4.0 (for Fe based clays) and pH 5.0–5.5 (for Cu based clays), 20 °C, 3 h reaction time	[96]
Al,Cu-PILC.bnt (0.6 wt.% Cu)	37	0		
Al,Fe-PILC.bnt (13.7 wt.% Fe)	100	50		
Al,Fe-PILC.bnt (28.2 wt.% Fe)	96	45		
Al-PILC.mont ^c (14.9 wt.% Al)	15 ^e	nd		
Al,Cu-PILC.mont (1.2 wt.% Cu)	70	5		
Al,Fe-PILC.mont (19.2 wt.% Fe)	100	66		
Al,Fe-PILC.mont (28.2 wt.% Fe)	100	70		
	96 (3 h)	nd	Fe/substrate molar ratio 10, 0.8 mM cinnamic acid, 66.4 mM H ₂ O ₂ , 80 °C, pH 2.9	[97]
Fe-PILC (22.3 wt.% Fe)	~91 (3 h)	nd	as above, but pH 4	
	89 (3 h)	nd	as above, but pH 5	
	90 (1 h)	nd	as above, but pH 2.9 and Fe/substrate molar ratio 2	
Bentonite clay				
Al,Cu-PILC (0.67 wt.% Cu)	10< (1 h)	10 (2 h)	Catalyst 5 g L ⁻¹ , 0.5 mM phenol, 2 mL h ⁻¹ H ₂ O ₂ (0.1 M), airflow (2 L h ⁻¹ in 100 mL phenol solution), pH 5.5, 20 °C as above, pH 3.7	[55]
Al,Fe-PILC (4.91 wt.% Fe)	90 (1 h)	60 (2 h)		
Al,Cu-PILC 0.67 wt.% Cu)	40 (1 h)	40 (2 h)	Catalyst 5 g L ⁻¹ , 0.5 mM phenol, 5 mM H ₂ O ₂ , 5 bar (air pressure), 40 °C, pH 5.5	
Al,Fe-PILC (4.91 wt.% Fe)	100 (<0.5 h)	40 (2 h)	As above, but pH 3.7	
Al,Fe-PILC (4.91 wt.% Fe)	20 (1 h)	10 (1 h)	As above, but pH 4.8–5.0	
	100 (1 h)	63 (2 h)	Catalyst 1 g L ⁻¹ , 0.5 mM phenol, 2 mL h ⁻¹ H ₂ O ₂ (0.2 M), airflow (2 L h ⁻¹ in 100 mL phenol solution), pH 3.7, 20 °C	
	58 (1 h)	62 (2 h)	As above, but H ₂ O ₂ (0.1 M)	
	100 (1 h)	67 (4 h)	As above, but 25 °C	
	100 (1 h)	78 (4 h)	As above, but 70 °C	
Natural clay (calcined; 5.6 wt.% Al, 1.7 wt.% Fe)			Catalyst 1.5 g L ⁻¹ , 0.22 mM phenol, 4 mM H ₂ O ₂ (1.3 stoichiometric amount for total mineralization), 28 °C, pH 4.0 (constant), 1.25 h reaction time	[72]
Fe,Al-PILC (9.2 wt.% Al, 1.3 wt.% Fe)				
Fe,Al-PILC (8.1 wt.% Al, 3.0 wt.% Fe)	~17	nd	As above, but pH 4.7 and 2 h reaction time	
Fe,Al-PILC (6.7 wt.% Al, 5.5 wt.% Fe)				
Fe,Al-PILC (5.5 wt.% Al, 7.5 wt.% Fe)	~80	nd		
Fe,Al-PILC (4.8 wt.% Al, 10.0 wt.% Fe)				
Fe,Al-PILC (4.3 wt.% Al, 11.5 wt.% Fe)	~90	nd		
Fe,Al-PILC (6.7 wt.% Al, 5.5 wt.% Fe)	~30	nd		
	<10	nd		
	<10	nd		
	~17	nd		
Natural clay	~15 (2 h)	~10 (4 h)	Catalyst 0.5 g L ⁻¹ , 0.5 mM phenol, 100 mM H ₂ O ₂ , pH 3.7, 20 °C	
Al-PILC (5.9 wt.% Fe)	~100 (2 h)	~38 (4 h)		[74]
Al-Ce-Fe-PILC (0.1 and 8.6 wt.% Ce and Fe respectively)	~100 (2 h)	~55 (4 h)		

Table 3 (Continued)

Catalyst	Catalytic activity		Reaction conditions	Ref.
	Substrate conversion (%)	TOC decrease (%)		
Al-PILC (2.45 wt.% Fe)	100 (4 h)	35 (4 h)	Catalyst 5 g L ⁻¹ , 0.5 mM phenol, 2 mM h ⁻¹ H ₂ O ₂ , pH 3.7, airflow (2 L h ⁻¹), 25 °C	[98]
Al,Fe-PILC (2.67 wt.% Fe; 0.22% in the pillar)	100 (4 h)	51 (4 h)	As above	
Al,Fe-PILC (3.01 wt.% Fe; 0.56% in the pillar)	100 (4 h)	65 (4 h)	As above	
Al,Fe-PILC (3.01 wt.% Fe; 0.56% in the pillar)	100 (2 h)	78 (4 h)	As above, 70 °C	
	100 (1.5 h)	78 (4 h)	Catalyst 10 g L ⁻¹ , 0.5 mM phenol, 4 mM h ⁻¹ H ₂ O ₂ , pH 3.7, airflow (2 L h ⁻¹), 70 °C	
Al,Fe-PILC (3.01 wt.% Fe; 0.56% in the pillar)	95 (1.5 h)	80> (4 h)	2 mM h ⁻¹ H ₂ O ₂ , as above	
	75 (1.5 h)	80> (4 h)	1.6 mM h ⁻¹ H ₂ O ₂ , as above	[99]
	66 (1.5 h)	80> (4 h)	1 mM h ⁻¹ H ₂ O ₂ , as above	
Natural clay (calcinated; 6.61 wt.% Fe)	48	5	Catalyst 5 g L ⁻¹ , 0.5 mM phenol, 2 mL h ⁻¹ H ₂ O ₂ (0.1 M, for 4 h), pH 3.7, 2 L h ⁻¹ (to 100 mL solution), 25 °C, 4 h reaction time	
Al-PILC (12.48 wt.% Al)	100	39		
Al,Fe-PILC (8.76 wt.% Fe)	100	50		
Al,Ce,Fe-PILC (6.16 wt.% Fe; 0.13 wt.% Ce)	100	55		
Al,Ce,Fe-PILC (7.34 wt.% Fe; 0.13 wt.% Ce)	100	52		
Al,Ce,Fe-PILC (8.68 wt.% Fe; 0.10 wt.% Ce)	100	54		
Saponite clay				
Fe-PILC (from acetylacetonate Fe(III)) (26.2 wt.% Fe)	~95 (0.5 h)	~82 (4 h)	Catalyst 0.07 g L ⁻¹ , 0.1 mM orange II, 13 mM H ₂ O ₂ , pH 3, 73.6 °C	
	~5 (4 h)	~5 (4 h)	As above, but 6.4 °C	[54]
	~95 (2 h)	~78 (4 h)	As above, but 40 °C	
	~95 (2 h)	~75 (4 h)	As above, but 1.2 mM H ₂ O ₂	
	~95 (2 h)	~81 (4 h)	As above, but 24.8 mM H ₂ O ₂	
	nd	~65 (4 h)	As above, but 1.2 mM H ₂ O ₂ and N ₂ atmosphere	
Phenol hydroxylation using clays ^e				
Al-PILC_bnt ^b	37 → 66_CAT/34_HQ ^f		Catalyst 50 mg L ⁻¹ , 10.6 mmol phenol, 3.5 mmol H ₂ O ₂ , 10 mL H ₂ O ₂ , T 50 °C, 2 h reaction time	[100]
Al,Fe-PILC_bnt (10.27 wt.% Al; 3.49 wt.% Fe)	42 → 65_CAT/35_HQ			
Al-PILC_mont ^c	37 → 66_CAT/34_HQ		Microwave assistance improves conversion and selectivity	
Al,Fe-PILC_mont (10.13 wt.% Al; 2.67 wt.% Fe)	41 → 68_CAT/32_HQ			

^a Not determined: nd.^b Bentonite.^c Montmorillonite.^d Adsorption.^e When the term "Hydroxylation" is in the catalytic activity column indicates that Fenton reaction has been used as a synthetic method in order to obtain desirable products. In those cases, substrate conversion, as well as selectivity for the reaction products at the same time is indicated.^f CAT: catechol; HQ: hydroquinone.

Mg/Al-LDH in the carbonate form has been used as solid base catalyst to promote aldol condensation and other organic reactions [102,104–107]. However Mg/Al-LDHs does not exhibit activity as redox catalyst. This ability to promote redox reaction can be introduced in the hydrotalcite material by using a transition metal that can participate in redox reactions [102]. One of the advantages of hydrotalcites is the large percentage of transition metals that can have in its composition [102].

In this regard it has been reported [108] that Cu,Al-LDHs can promote Fenton hydroxylation of phenol to form dihydroxybenzenes accompanied by small amounts of benzoquinones [108–110]. Anal-

ogous LDHs containing Mg/Al, Zn/Al, Co/Al, Ni/Al do not exhibit any activity in this reaction [108] (see Table 4). This is again in agreement with the fact that besides iron species Fenton chemistry can be promoted by copper ions [48,91]. It has been found that the highest activity is achieved for a Cu/Al-LDH with a Cu/Al atomic ratio 4:1 that is the maximum percentage of copper achievable in LDHs [108]. It is important to note that the maximum activity was found at neutral pH, lower and higher values being less favourable due to the instability of the solid at low pH values or the preferential complexation of the active sites by HO⁻ rather than H₂O₂ at basic pH. The optimum conditions for the highest phenol conver-

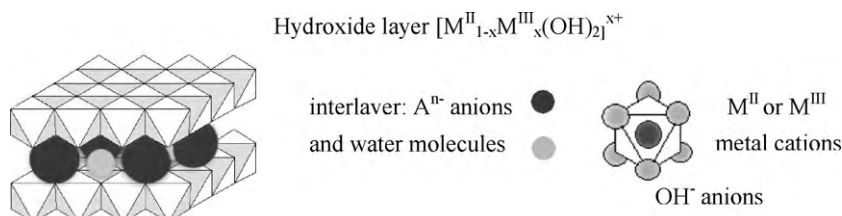


Fig. 8. Layered crystal structure of a hydrotalcite.

Table 4
Hydrotalcites as Fenton catalysts for the oxidation of phenol.

Catalyst	Substrate conversion (%)	Selectivity ^a (%)	Reaction conditions	Ref
CuMgAlCO ₃ -LDH	40.8	54.8.CAT/45.8.HQ/0.2.BQ	Catalyst 0.05 g, 0.5 g phenol (5.3 mmol, 25 mL H ₂ O), 318 mmol H ₂ O ₂ , 60 °C, 1 h reaction time, pH 7.	[108]
CuZnAlCO ₃ -LDH	38.4	57.4.CAT/42.4.HQ/0.2.BQ		
CuCoAlCO ₃ -LDH	44.9	57.2.CAT/42.6.HQ/0.2.BQ		
CuNiAlCO ₃ -LDH	47.1	51.9.CAT/47.9.HQ/0.2.BQ		
CuCuAlCO ₃ -LDH	53.5	59.0.CAT/36.0.HQ/5.0.BQ		
MgAlCO ₃ -LDH	0			
ZnAlCO ₃ -LDH	0			
CoAlCO ₃ -LDH	0			
NiAlCO ₃ -LDH	0			
CoAl-LDH (35.9 wt.% Co, 6.1 wt.% Al)	0	0.CAT/0.HQ ^a	Catalyst 0.01 g, 1 g phenol (10.6 mmol), 2.4 g H ₂ O ₂ (30%, 21.2 mmol), 10 mL H ₂ O, pH 5, 65 °C	[112]
CoNiAl91-LDH (35.9 wt.% Co, 6.1 wt.% Al; 3.1 wt.% Ni)	5.0	100.CAT		
CoNiAl21-LDH (25.6 wt.% Co, 6.6 wt.% Al; 12.0 wt.% Ni)	7.6	100.CAT		
CoNiAl11-LDH (19.1 wt.% Co, 6.5 wt.% Al; 18.6 wt.% Ni)	8.6	100.CAT		
CoNiAl12-LDH (13.5 wt.% Co, 6.2 wt.% Al; 22.4 wt.% Ni)	8.9	100.CAT		
CoNiAl15-LDH (5.9 wt.% Co, 6.2 wt.% Al; 22.4 wt.% Ni)	14.2	79.CAT/21.HQ		
CoNiAl19-LDH (3.1 wt.% Co, 6.1 wt.% Al; 31.3 wt.% Ni)	4.0	100.CAT		
NiAl-LDH (33.5 wt.% Al; 5.8 wt.% Ni)	0	0.CAT/0.HQ		

^a CAT: catechol; HQ: hydroquinone; BQ: benzoquinone.

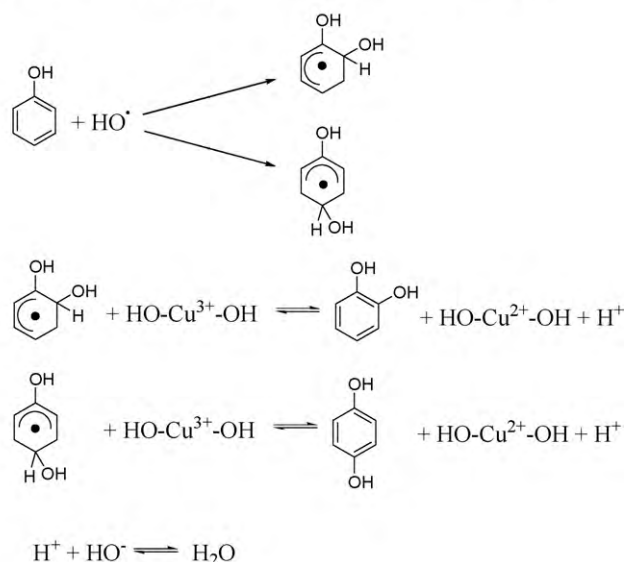
sion at 1 h reaction time were 60 °C in water at pH 7. Actually it was found that phenol hydroxylation does not occur in organic solvents. One fact that deserves especial comment is the use of a large molar excess of H₂O₂ (phenol/H₂O₂ molar ratio 1:60) to achieve a maximum phenol conversion of 56%. Considering that H₂O₂ is a relatively expensive commodity, it would be highly desirable to reduce the excess of H₂O₂ in order to make viable the process. Concerning the reaction mechanism, introduction of a hydroxyl group into an aromatic ring has been considered as a hallmark of the generation of hydroxyl radical. Thus, it is proposed that electron transfer between framework Cu²⁺ and H₂O₂ will generate Cu³⁺ and HO•. This high valence for copper ions is certainly uncommon. The cycle is closed when Cu³⁺ is reduced to Cu²⁺ by the cyclohexadienyl radical derived from phenol or by H₂O₂ forming O₂. Actually O₂ evolution was observed in the system. Scheme 3 illustrates the proposed reaction mechanism.

Chen et al. presented one of the few examples about regeneration of hydrotalcite-based catalyst [111]. The authors studied the deactivation and reactivation of copper-containing hydrotalcite (Cu-LDH) in the catalytic hydroxylation of phenol. The results show a conversion of phenol of 63% and selectivity above 95% for catechol + hydroquinone (see Fig. 9). However, Cu-LDH becomes deactivated after the first operation, and apparently deactivation occurs mainly due to the carbon deposition on the catalytic surface. The deactivated catalyst can be easily reactivated by burning deposited carbon in air and subsequent washing with acetone. It was found that the reactivated catalyst maintains the crystal structure and shows almost the same catalytic performances as the fresh hydrotalcite (see Fig. 9). This is, nevertheless, surprising since it is a well-known fact that hydrotalcites are thermally labile and they lose their characteristic layered structure upon calcination at temperatures about 400 °C (see below for the Cu,Ni,Al-LDH) [80].

Besides Cu-LDH, other LDH materials containing cobalt and nickel metals have also been used as solid catalysts for the Fenton reaction [108,112]. Table 4 summarizes some of the data reported.

Hydrotalcites have been used as support of sulfonated iron phthalocyanine (FePcSO₃[−]) [113]. Depending on the Mg to Al ratio, FePcSO₃[−] is present as monomeric μ-oxo complex or dimeric non-

Main reactions



Side reactions



Scheme 3. Proposed radical substitution mechanism for the phenol hydroxylation, catalyzed by Cu/Al-LDHs.

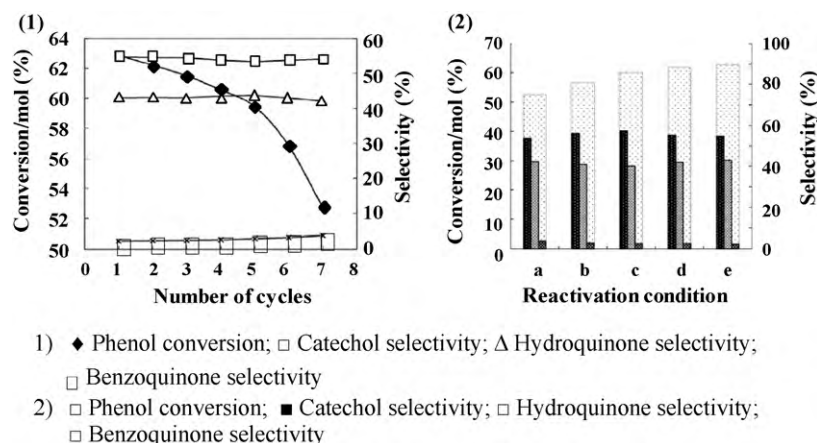


Fig. 9. 1) Performance of Cu-LDH as catalyst for phenol hydroxylation upon use; 2) Reactivation of the deactivated catalyst. (a) The deactivated catalyst without treatment, (b) calcination under low temperature, (c) washing with acetone, (d) burning deposited carbon in air and subsequent washing with acetone and (e) the fresh catalyst (figure taken from ref. [111]).

oxo-bridge FePcSO_3^- . These samples were tested for the oxidation of catechol (50 mM) at pH 10 at 30 °C by H_2O_2 (17-fold in excess). When the reaction is performed with the FePcSO_3^- in homogeneous condition, a relatively low conversion of catechol (21%) under the reaction conditions was observed. This low activity of dissolved FePcSO_3^- was explained considering that FePcSO_3^- becomes deactivated by formation of dimeric/oligomeric μ -oxo-bridge species that are inefficient to promote the reaction. However, when incorporated in Mg/Al, hydrotalcite immobilization of the supported FePcSO_3^- site makes difficult this deactivation mechanism and the FePcSO_3^- becomes notably more active. Importantly depending on the speciation of the FePcSO_3^- it was observed that the Mg/Al ratio of the hydrotalcite influences the catalytic activity, reaching an activity about 4 times higher than the same complex concentration in solution [113]. Blank controls using Mg/Al hydrotalcites without FePcSO_3^- reveals that the support is almost devoid of any catalytic activity in the absence of FePcSO_3^- . The previous results clearly exemplifies a general benefit of adsorbing active metallic complexes on inert support to minimize deactivation processes derived from aggregation of the species in solution.

One of the advantages of hydrotalcites is that these materials can also be obtained having homogeneously distributed in their structure more than one, di- or trivalent cation. In this context Kannan and co-workers [114] have reported the synthesis of ternary hydrotalcites containing Cu, Ni and Al and have used them for the liquid phase hydroxylation of phenol. In a certain way, these ternary hydrotalcites resemble the pillared clays in which the composition of the pillar contains several metals. As in the case of pillared clays, ternary hydrotalcites must be carefully surveyed for the presence of several phases in which different metals predominate instead of being forming a single solid phase. Several parameters including the substrate to catalyst ratio, the substrate to oxidant ratio (higher conversion in the presence of higher amount of oxidant), the substrate to H_2O_2 molar ratio, the reaction temperature and the hydrotalcite composition were studied [114]. Surprisingly and in a counter intuitive way it was observed that the conversion of phenol increases along the substrate to catalyst ratio. Thus, higher phenol conversions up to 23.7% were obtained when the substrate to catalyst ratio was increased up to 100. It was suggested that when the amount of catalyst was too high spontaneous formation of coke leading to catalyst inactivation occurs [114].

However, this explanation is not totally convincing since it is expected that the same coke will be also formed, even more spontaneously, when higher amounts of phenol are also present and less catalyst is present in the reaction. It is, however, more reasonable to attribute this deactivation under phenol defective conditions

to multiple consecutive oxidations due to over oxidation leading to poisonous by-products that will not be formed when the large excess of phenol minimizes consecutive over oxidation. In any case, it would be of interest to revisit these data and determine why performing in the presence of larger amount of hydrotalcite can be unfavourable for the reaction. Particularly, it should be checked that hydrotalcite is not causing the spurious decomposition of hydrogen peroxide and it is the lack of oxidizing reagent what causes the apparent decrease in catalytic activity.

It is known that the thermal stability of the hydrotalcites is very limited and that beyond 400 °C the layered structure collapses and formation of different oxides or even mixed metal oxides phases appear [80]. For the ternary Cu, Ni, Al hydrotalcites it was found that the catalytic activity for promoting the Fenton reaction ceases when these hydrotalcites are submitted to calcination at temperatures in the range of 150–800 °C [114]. As expected it was observed that XRD of the layered structure disappears above 400 °C.

The most interesting point of the work was the observation of some variation in the catalytic activity, depending on the Ni, Cu, Al ratio of the material [114]. However since the most active hydrotalcite of the series $([\text{Ni}_{0.14}\text{Cu}_{0.61}\text{Al}_{0.25}(\text{OH})_2](\text{CO}_3)_{0.13} \cdot 0.96\text{H}_2\text{O})$ was the one with the highest Cu content (23.7% phenol conversion at 65 °C in 2 h using a phenol/ H_2O_2 molar ratio of 2), it would have been of interest to include in the study a binary hydrotalcite containing exclusively Cu, Al.

Continuing with the catalytic activity of ternary hydrotalcites [115] other samples containing Cu as well as Ni or Co as divalent cation and Al, Cr or Fe as trivalent cation have been also prepared and tested, but their catalytic performance does not increase with respect to that of Cu, Ni, Al with $[\text{Ni}_{0.14}\text{Cu}_{0.61}\text{Al}_{0.25}(\text{OH})_2](\text{CO}_3)_{0.13} \cdot 0.96\text{H}_2\text{O}$ composition.

As a general comment, the most interesting feature of hydrotalcites as Fenton catalysts is that these materials are active at neutral or quasi neutral pH.

9. Zeolites

9.1. Structure

Zeolites are crystalline aluminosilicates whose structure defines channels and cages termed as micropores that are open to the external surface of the particle allowing mass transfer from the exterior to the interior of the crystal [116,117]. Depending on the dimensions of the micropores, the zeolites are generally classified as small, medium and large pore size when the channels are constituted by eight, ten and twelve oxygen atoms, respectively. The

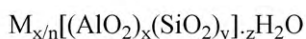
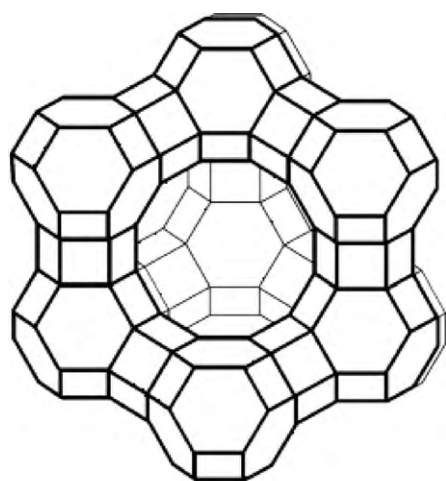


Fig. 10. General formula of zeolites and structure of zeolite Y.

open porosity determines that the surface area of the zeolites is very large compared to non-porous materials [117]. As in the case of clays, the presence of aluminium replacing isomorphically a silicon atom introduces a net negative charge in the framework per aluminium atom that requires the presence of charge balancing cations to ensure the electroneutrality of the solid. Fig. 10 presents the general formula of zeolites as well as the pore system of some of the most widely used zeolites.

Due to the ionic bonding between the charge compensating cation and the rigid zeolite framework it is possible to effect the metathesis of one cation by another without producing any alteration of the rigid framework [116,117]. Typically the charge balancing cations are alkali metal ions but they can be replaced by other mono-, di- and even tripositive organic or inorganic ions [118]. A special case is when protons are the compensating cations giving rise to the acid form of zeolites [119]. Actually zeolites are widely used as solid acids in large-scale industrial processes and are among the most important heterogeneous catalyst including as oxidation catalysts [116,117,120].

No surprisingly, zeolites have also been used as heterogeneous Fenton catalysts. The obvious materials to be tested are the most common zeolites ion exchanged with iron.

9.2. Zeolites as Fenton catalysts

9.2.1. ZSM5

Most of the work on the development of solid Fenton catalysts has been carried out using phenol disappearance as parameter to quantify the efficiency of the process. In an alternative study Centi et al. [121] have used propionic acid, a considerably more reluctant compound for degradation, as probe molecule to test the catalytic activity of Fe^{3+} -exchanged ZSM5 (2.34 wt.% Fe). Comparison of the activity of homogeneous and heterogeneous catalysts for similar iron contents has established that the homogeneous catalyst exhibits higher reaction rate for TOC reduction at lower H_2O_2 consumption. Considering that H_2O_2 is a costly commodity high consumption, as for the Fe-ZSM5 catalyst, is unfavourable and should be minimized unless is accompanied by a parallel decomposition of the organic pollutant.

One interesting observation was, however, that the catalytic activity of the homogeneous catalyst is more sensitive to the solution pH than the heterogeneous Fe-ZSM5 solid [121]. This fact makes Fe-ZSM5 the preferred catalyst under some circumstances.

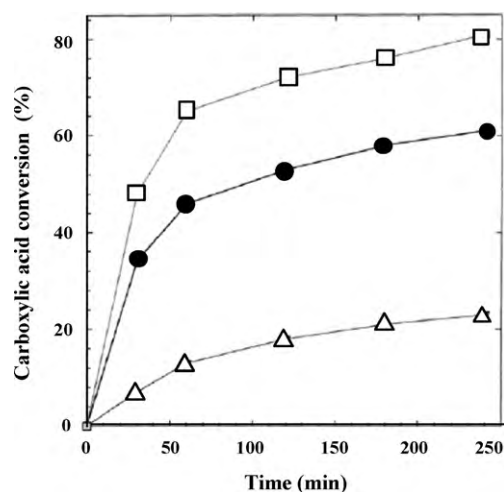


Fig. 11. Conversion of propionic, acetic and formic acids as a function of the time of reaction (pH 4, H_2O_2 /substrate = 1.5, 0.1 g Fe-ZSM5). □ Propionic acid; ● Formic acid; △ acetic acid (figure taken from ref. [121]).

As it could be anticipated an increase in the temperature in the range of 50–70 °C increases conversion of propionic acid reducing the time to achieve a certain conversion level. Although leaching from the zeolite to the liquid phase was observed, the concentration of Fe leached is not responsible for the catalytic activity observed for Fe-ZSM5. The percentage of iron leaching increases with the temperature and with the amount of H_2O_2 present in the solution. However, due to the small percentage of iron leached (up to 7% at 70 °C) the catalyst can be reused and shows good stability provided that the material is calcined at 500 °C before reuse. Most zeolites, but particularly ZSM5 are remarkably stable upon calcination. One additional interest of the work is that attention has been paid to the consumption of H_2O_2 and that the excess of this reactant has been limited during the test to a relatively low excess. Compared to propionic acid, formic acid and particularly acetic acid are even more difficult to decompose by the Fenton reaction and these two acids are in fact accounting for the residual TOC after disappearance of propionic acid [121]. To illustrate the difference in the rate of decomposition using Fe/ZSM5, Fig. 11 shows the time-conversion plot for the degradation of propionic, acetic and formic acid using Fe-ZSM5 as catalyst under the same conditions.

Overall this report [121] using a commonly available commercial ZSM5 zeolite and performing a simple ion exchange serves to illustrate the similar performance of homogeneous and heterogeneous iron catalysts for the degradation of carboxylic acids that are ubiquitously present in waste waters and also are formed as by-products in the degradation of other organic molecules.

Similar conclusions about the activity of Fe-ZSM5, in this case for the decomposition of ethanol, were obtained by Kuznetsova et al. [122] who determined that the leaching of iron, even in the presence of complexing agents such as $P_2O_7^{4-}$ does not account for the catalytic activity of the solid. However in this case, the difference in the catalytic activity between $Fe(NO_3)_3$ in homogeneous phase and Fe-ZSM5 was notable and it was attributed to the possible lower redox potential of the iron ions inside zeolite (see Fig. 12).

Although this assumption of lower oxidation potential was not proved, it was assumed that the lack of activity of Fe-phosphate complex compared to aquated Fe^{3+} ions is also due to this decrease of the oxidation potential of the Fe-phosphate complex compared to aquated Fe^{3+} . Since oxidation potential values can be easily measured by several electrochemical techniques, it would have been more convenient to support experimentally the proposal to rationalize the decrease of the catalytic activity data upon complexation with the set of oxidation potentials. This study clearly demonstrates

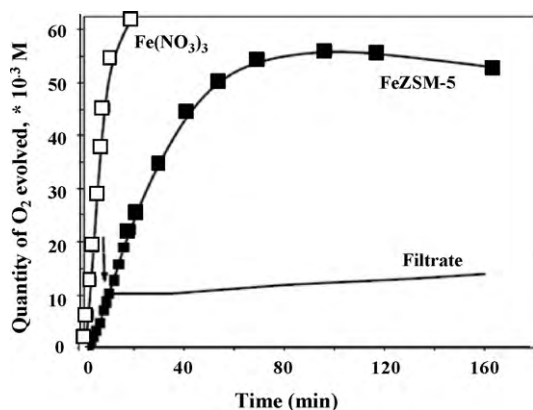


Fig. 12. The kinetics of the O_2 release from the 5 mM $Fe(NO_3)_3$ solution (\square), 15 g L $^{-1}$ suspension of the Fe-ZSM5 (3.5 wt.% Fe) (\blacksquare) and its filtrate (line without symbols). An arrow shows the moment of the filtration. Temperature 35 °C, $[H_2O_2] = 0.1$ M (figure taken from ref. [122]).

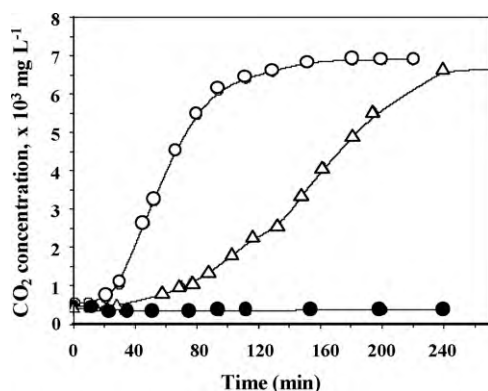


Fig. 13. Kinetics of 5.8 mM C_2H_5OH oxidation by 0.4 M H_2O_2 in the presence of a 15 g L $^{-1}$ suspension of Fe-ZSM5 (3.5 wt.% Fe) without salt (\circ) and in the presence of 0.5 M KCl (\triangle) and 36 mM $Na_4P_2O_7$ (\bullet) (figure taken from ref. [122]).

that the catalytic activity of an iron exchanged ZSM5 is decreased, and even totally quenched, by the presence of inorganic salts in the solution. The presence of these inorganic salts also strongly influences the Fe^{3+} leaching [122]. Fig. 13 shows the temporal profile of CO_2 evolution (equivalent to ethanol mineralization) in the absence and in the presence of KCl and $Na_4P_2O_7$. This observation of activ-

ity quenching by the presence of inorganic salts in the medium certainly merits a convincing rationalization, since it could reflect the occurrence of Fe^{3+} leaching followed by complexation, but also it could be due inactivation of hydroxyl radicals by the inorganic salts. It is known that PO_4^{3-} , CO_3^{2-} , SO_4^{2-} , ClO_4^- , Cl^- and other inorganic anions react with $HO\bullet$ radicals and can quench the Fenton reaction [123–131]. However, in general from the high amount of catalyst employed (15 g L $^{-1}$) and the high excess of H_2O_2 employed in this study, it appears that the process is not very efficient even in the absence of inorganic salts.

Fajerwerg and Debellefontaine [132] have performed a study of the degradation of phenol by H_2O_2 in the presence of a series of solid catalysts containing iron, copper, manganese and titanium or a combination of iron, copper and manganese. The materials were prepared by impregnation or ion exchange but the nature of the actual metal salts employed in the catalyst preparation has not been disclosed. Besides iron phosphates the study includes silica, silica-alumina and zeolites Y and ZSM5 as support for the transition metals. The experimental conditions to test the relative efficiency of the various catalysts employed were 6.5 g L $^{-1}$ of phenol and 21 equivalents of H_2O_2 in the presence of 0.35 g L $^{-1}$ of catalyst. The degradation is carried out at 70 °C and the initial pH value for most of the reactions was 5 and was free during the course of the degradation. This large excess of H_2O_2 (21 equivalents) was estimated as 1.5 times the required amount to convert all the phenol carbons into CO_2 . One point of concern is that given that the amount of transition metal per gram of catalyst varies considerably from 0.9% to 27%, the use of a fixed weight of catalyst to compare the catalytic activity for those catalysts can be unfair for those materials in where the iron content is small. Actually the turnover number, i.e. the moles of phenol converted per mol of transition metal, should be the figure of merit to establish a more balanced comparison. Table 5 shows some selected values of the reported activity data for the phenol degradation in the presence of the transition metal catalyst.

Considering the preparation procedure (impregnation or ion exchange), it is not surprising that the authors observe metal leaching from the solid to the solution. This leaching is highly detrimental in heterogeneous catalysis since it causes the gradual deactivation of a catalyst due to the depletion of active sites. Also the leached metal can mask the real activity of the solid because it can contribute to the overall activity observed. It would have been desirable to report data of the relative contribution of the homogeneous catalysis due to leaching versus the total catalytic activity. Actually when the transition metal loading is high, the main role of the

Table 5

Oxidation of phenol by various heterogeneous catalysts, TOC[phenol] = 69 mM, catalyst 0.35 g L $^{-1}$, H_2O_2 21 equivalents (1.5 stoichiometric ratio for complete CO_2 mineralization), initial pH 5, 10^5 Pa, reaction time 90 min, 70 °C.

Catalyst	Nature of catalyst	Active metal (wt.%)	% TOC removal	% H_2O_2 decomposition
Cu-NaY	Zeolite-Y ^a	Cu (2)	11	59
Cu- NaY	Zeolite-Y ^a	Cu (5)	19	37
Cu,Mn- NaY	Zeolite-Y ^a	Cu (4.6), Mn(2)	69	88
Fe,Cu,Mn-aerosil-200	Nanoparticles silica ^b	Fe (1.25) Cu (2.5) Mn (1.25)	21	33
Fe,Cu,Mn-SiO ₂ -Al ₂ O ₃	Silica-alumina ^b	Fe (1.25), Cu (2.5) Mn (2.5)	51	47
Fe-aerosil 200	Silica ^a	Fe (1.5)	35	30
FePO ₄	Phosphate	Fe (37.1)	41	72
Fe ₃ (PO ₄) ₂ ·8H ₂ O	Phosphate	Fe (33)	45	54
Fe-ZSM5	Zeolite-ZSM5 ^c	Fe (2)	24	35
H-Fe-silica	Silica	Fe (0.9)	0	22
TS-1	Zeolite silicate ^c	Ti (1.5)	0	18
Fe ₂ O ₃	Aerogel	Fe (70)	8	15
KFeP ₂ O ₇	Insoluble phosphate	Fe (21)	4	20
Na ₂ Fe ₅ Si ₈ O ₂₂ (OH) ₂	Silicate	Fe (32)	3	24
RbFeP ₂ O ₇	Insoluble phosphate	Fe (18)	5	10

Table adapted from ref. [132].

^a Ion-exchange method.

^b Impregnation method.

^c Hydrothermal method.

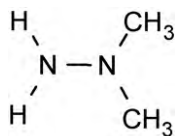


Fig. 14. 1,1-Dimethylhydrazine (UDMH) chemical structure.

solid could be simply to provide a steady concentration of the metal in solution. In any case, it was proposed that iron impregnated ZSM5 was the catalyst of choice, preferred to other iron containing zeolites, silicas and phosphates and also preferred to copper and manganese containing materials [132].

As commented earlier most of the studies of the Fenton reaction catalyzed by solids use phenol as probe molecule. Degradation of other toxic organic compounds has received considerably less attention. In one interesting study decomposition of 1,1-dimethylhydrazine (UDMH) by H_2O_2 in the presence of Fe-exchanged ZSM5 (2.4 wt.% Fe) has been reported [51]. UDMH (see Fig. 14) is the principal component of liquid rocket propellers and due to its toxicity (most basic nitrogen compounds are highly undesirable) its concentration in water is limited to $10 \mu\text{g L}^{-1}$. Thus, it appears that degradation of UDMH can be a real problem in specific industries.

The major problem of Fenton reaction is that only a small percentage of the total H_2O_2 consumption is converted into free $\text{HO}\cdot$ (see Eqs. (1)–(7)). Through different pathways (mainly H_2O_2 dismutation) most of the H_2O_2 is finally converted into molecular oxygen (see Eq. (6)). This process leading to O_2 corresponds to a spurious waste of H_2O_2 , a commodity whose cost is relatively high.

One of the ways in which useless decomposition of H_2O_2 takes place is by self-quenching of $\text{HO}\cdot$ radicals by H_2O_2 according to Eq. (5).

This process can be part of the overall generation of oxygen and is kinetically favourable. Formation of hydroperoxyl radicals can prevail when the concentration of H_2O_2 is high. Hydroperoxyl radicals are considerably less reactive than the free $\text{HO}\cdot$ [18]. For this reason, in the case of the H_2O_2 decomposition of UDMH using $\text{Fe}(\text{NO}_3)_3$ in homogeneous phase it was found that the initial reaction rate of CO_2 evolution (taken as indication of the occurrence of Fenton chemistry) is constant for H_2O_2 concentration in the range of 0.2–4 M showing that an increase of H_2O_2 in this concentration range has virtually no effect on the efficiency on the Fenton chemistry [51]. In contrast to this behaviour observed in the homogeneous phase, the use of Fe-ZSM5 as heterogeneous catalyst leads to a different behaviour with an increase in the initial CO_2 evolution reaction rate along the H_2O_2 concentration. Fig. 15 shows the contrasting behaviour observed in homogeneous and heterogeneous Fenton for the degradation of UDMH as a function of the H_2O_2 concentration in the solution. This favourable feature of Fe-ZSM5 has been attributed to the adsorption of the organic nitrogen compound inside the zeolite micropores resulting in an increase of the effective organic concentration near the catalytic site (estimated as 32-fold concentration inside zeolite micropores with respect to the solution concentration according to independent studies of the isothermal adsorption).

Another advantage Fe-ZSM5 as heterogeneous catalyst compared to homogeneous ferric ions is that in the case of Fe-ZSM5 the iron ions do not undergo undesirable complexation with formic or acetic acids that eventually are not further transformed into CO_2 . Therefore the system $\text{H}_2\text{O}_2/\text{Fe-ZSM5}$ promotes mineralization and larger decrease in the TOC value for UDMH degradation than the homogeneous Fenton reaction [51]. However as a general remark we have to indicate that UDMH decomposes in a significant extent at pH 12 in the presence of H_2O_2 even in the absence of any cata-

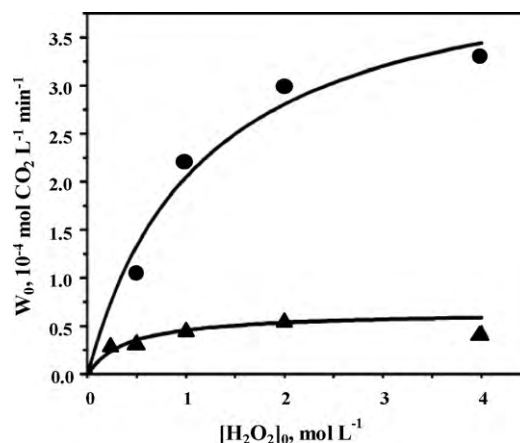


Fig. 15. Dependence of the initial UDMH oxidation rate (W_0) on the H_2O_2 initial concentration in 5 mM $\text{Fe}(\text{NO}_3)_3$ solution (▲) and 16 g L^{-1} Fe-ZSM5 suspension (●) at 25°C , $[\text{UDMH}]_0 = 10 \text{ mM}$ (figure taken from ref. [51]).

lyst. Catalysis is only necessary and most efficient in the range of pH values from 2 to 7.

9.2.2. Zeolite Y

Besides phenol degradation, decoloration of persistent dyes used in the textile industry has also been a very common test to assess the activity of Fenton processes and catalyst. In this regard it has been reported [52] that iron-exchanged Y zeolite is a heterogeneous catalyst for the degradation of reactive azo dyes by H_2O_2 . As starting material a dealuminated ultra-stable zeolite Y was selected and submitted to three consecutive ion exchanges with 1 M aqueous solution of $\text{Fe}(\text{NO}_3)_3$ at 80°C . Unfortunately the experimental procedure does not mention the pH of the ion exchange that, apparently, was uncontrolled. Under uncontrolled pH and considering speciation of Fe^{3+} in water at different pH values, the prevailing species may not be hydrated Fe^{3+} , but $\text{Fe}(\text{OH})_2^{2+}$ and $\text{Fe}(\text{OH})_2^+$ depending on the pH value. Therefore, these hydroxy iron (III) cations are the species that are most likely introduced during the ion exchange. The problem is that these hydroxy compounds can easily oligomerize inside the zeolite micropores leading to iron oxide clusters depending on the aging whose composition and catalytic performance is difficult to reproduce and, in any case, can be different from the activity of solvated Fe^{3+} . Using this FeY zeolite sample (1.69 wt.% Fe) as solid Fenton catalyst for the decoloration of reactive azo dye Procion Marine H-EXL by H_2O_2 , a study of the influence of the initial pH in the range 2–8 on the activity was undertaken [52]. Since no buffers were used, the initial pH of the solution decreases over the reaction time, this leading to a complete decoloration in all cases after 60 min independently of the initial pH. This decrease of the pH value over the time is most probably due to the generation of acids from the degradation of the dye.

Leaching of iron species from the zeolite to the solution was observed, particularly at acid pH [52]. Nevertheless, the material was reused for a second run, essentially with the same catalytic performance as the fresh material. It can be, however, assumed that upon consecutive reuses leaching of iron will cause eventually a depletion of this metal in the zeolite and, therefore, the catalytic performance of the material will decrease. Maintaining constant the concentration of dye and H_2O_2 as well as other reaction conditions, the influence of the amount of iron zeolite on the color removal of the solution containing Procion Marine was determined [52]. Analogously the influence of the H_2O_2 concentration in the range from 10 to 35 mM on the decoloration of Procion Marine was also addressed. It has to be, however, commented that the

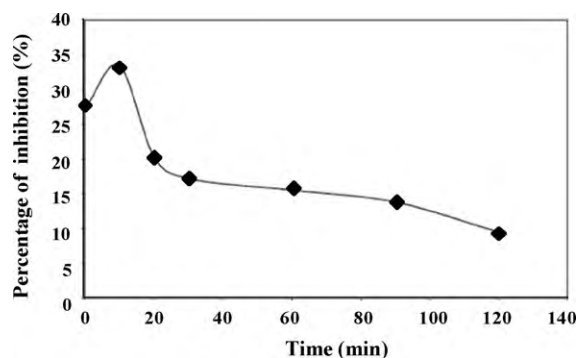


Fig. 16. *Vibrio fischeri* inhibition percentage after 15 min incubation by the bacteria in the presence of Procion Marine H-EXL azo dye. Initial conditions: 100 mg L⁻¹ azo dye, initial pH 5, $T=50^{\circ}\text{C}$, catalyst concentration 1 g L⁻¹ and 20 mmol L⁻¹ H₂O₂ (figure taken from ref. [52]).

optimum catalyst and H₂O₂ amount will strongly depend on the concentrations of the substrates and reagent and therefore it cannot be extrapolated to other reaction conditions. Working with 100 mg L⁻¹ azo dye at initial pH 5 and 50 °C in the presence of 1 g L⁻¹ of FeY (Si/Al molar ratio 5.75) and 20 mM H₂O₂, 98.9% color removal, 39.3% TOC reduction and 81.3% H₂O₂ decomposition were achieved after 60 min reaction time [52]. Using high performance ion chromatography the presence of acetate, nitrate, formate, malonate and oxalate was detected as the main oxidation products. Importantly the toxicity of the solution during the course of the Fenton reaction was determined using the bioluminescence of *Vibrio fischeri* as toxicity test [52]. It was observed that at short reaction times the toxicity of the solution even increases with respect to the initial azo dye solution but over the course of the reaction the toxicity becomes significantly reduced. Fig. 16 shows the evolution of the inhibition of *Vibrio fischeri* during the course of the Fenton treatment. When the performance of FeY zeolite was compared to Fe³⁺ in homogeneous solution it was found that the heterogeneous catalyst exhibits higher activity for color removal than Fe³⁺ at the same concentration in homogeneous phase. Fig. 17 shows the temporal profiles of the dye degradation under homogeneous and heterogeneous catalysis. No reasons for the higher activity of Fe zeolite are given. This result is somehow surprising since the azo dye is not adsorbed in the zeolite and also is too large to enter the zeolite pores. It could be however possible that in the control experiment the initial pH of the experiment in homogeneous phase (pH 5) causes partial precipitation of iron. Formation of colloidal iron

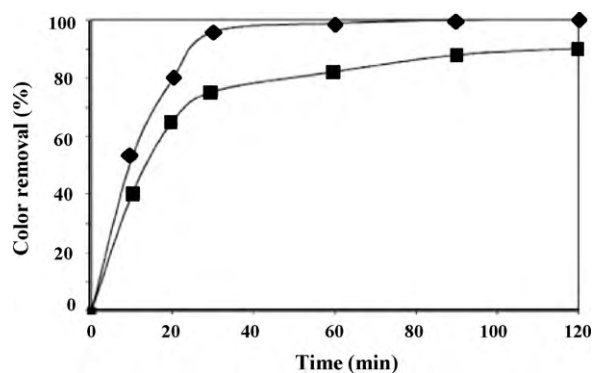


Fig. 17. Catalytic wet peroxide oxidation of Procion Marine H-EXL at 50 °C, pH 5 and 20 mmol L⁻¹ H₂O₂ using 1 g L⁻¹ FeY (Si/Al molar ratio 5.75) (♦) and Fe³⁺ ions (3.02 mM) in solution as catalysts (■) (figure taken from ref. [52]).

oxide would be difficult to be observed in a solution having strong color and will be undetected.

This catalyst was also tested for the treatment of a model solution containing Procion Marine H-EXL dye simulating a textile waste water and determining the color removal and chemical oxygen demand (COD) of the solution [52]. It was observed that at pH 5, 50 °C using 5-fold mol excess of H₂O₂ and almost complete color removal and 82% of COD was achieved.

Analogous work was also extended by studying the influence of the Si/Al molar ratio of the iron exchanged zeolite [133]. In catalysis it is well-known that the framework Si/Al ratio controls the activity of the zeolites by modifying the density of the sites (the presence of framework Al introduces a negative charge in the lattice), the strength of the site, hydrophobicity/hydrophobicity of the micropores and even the stability of the sites and their tendency to undergo deactivation [134]. In this sense, it is very common that zeolites with the same structure (Faujasite Y) and nature of the sites (Fe³⁺) exhibit different catalytic activity and different turn over number (TON) depending on the Si/Al ratio. The TON corresponds to the molecules degraded per active site in a certain reaction time. In the present study the activity of three Y zeolites with framework Si/Al ratio 2.6, 5.75 and 40 was tested [133]. The results were compared for the degradation of Reactive Yellow 84 azo dye (see Fig. 18).

The results are summarized in Table 6 in where the iron content and TON are also given. As it can be seen in this Table, the zeolite with higher Fe³⁺ content exhibits the best performance. However when the activity per iron atom is determined (TON), then the dealuminated zeolite Y (Si/Al molar ratio 5.75) exhibits the highest

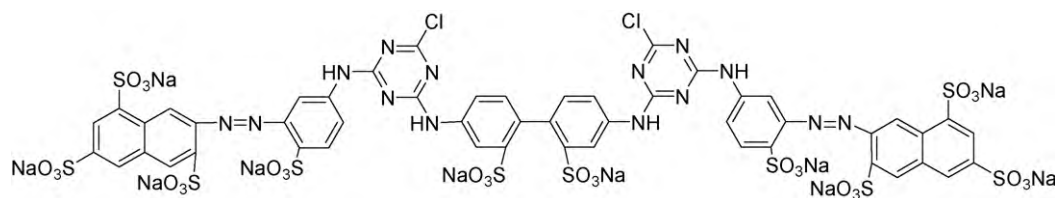


Fig. 18. Chemical structure of Reactive Yellow 84 azo dye.

Table 6

Evaluation of the catalytic performance of three iron exchanged ultra-stable Y zeolites in the wet H₂O₂ oxidation of reactive Yellow 84^a.

Catalyst (Si/Al molar ratio)	Color removal (%)	COD removal (%)	TOC removal (%)	H ₂ O ₂ decomposition (%)	Iron content (wt.%)	Iron leached (%)	TON ^b
FeY(2.6)	99.96	>74.14	60.80	41.67	2.76	8.91	3.2
FeY(5.75)	97.83	>74.14	51.57	44.00	1.69	11.54	4.4
FeY(40)	78.87	38.60	10.00	23.61	0.56	5.30	2.6

Table adapted from ref. [133].

^a Initial conditions: 100 mg L⁻¹ (2.60 mM TOC) dye, 1 g L⁻¹ catalyst, 20 mM H₂O₂, pH 5, $T=50^{\circ}\text{C}$, reaction time 2 h.

^b TON: mM of degraded carbon/mM of initial iron.

Table 7Catalytic properties of different Fe-containing materials for wet peroxidation of phenolic solutions^a.

Catalyst	X_{TOC}^b (%)	$X_{\text{H}_2\text{O}_2}^c$ (%)	pH ^d	Leaching test		
				[Fe] _{catalyst} ^e	[Fe] _{dissolved} ^f	Fe (%)
Direct synthesis						
Fe-TS-1 (0.64 wt.% Fe)	64.1	100	2.89	3.8	0.6	15.7
Fe-TS-1 (1.18 wt.% Fe)	66.0	100	2.76	7.1	1.3	18.3
Fe-TS-1 (4.43 wt.% Fe)	70.7	100	3.08	26.2	11.1	42.4
Fe-silicalite (3.64 wt.% Fe)	79.1	100	3.21	21.8	9.4	43.1
Fe-ZSM5 (2.48 wt.% Fe)	68.2	–	3.11	14.8	14.1	95.3
Ion exchange						
Fe-NaY (1.29 wt.% Fe)	78.5	95.7	4.74	7.6	2.1	27.6
Fe-USY (1.08 wt.% Fe)	67.3	–	4.67	6.4	3.7	57.8
Fe-ZSM5 (0.33 wt.% Fe)	54.5	–	–	2.3	1.7	73.9

Table adapted from ref. [135].

^a Reaction conditions: initial $\text{TOC}_{[\text{Ph-OH}]}$ = 765 mg L⁻¹; stoichiometric amount of H_2O_2 for phenol mineralization (14 equivalents); catalyst concentration = 0.6 g L⁻¹; initial pH 5.6; temperature = 100 °C; air pressure = 1 MPa; reaction time = 120 min.^b TOC conversion defined as (initial TOC – final TOC)/initial TOC × 100.^c H_2O_2 conversion defined as (initial oxidant – final oxidant)/initial oxidant × 100.^d Final pH after reaction.^e Milligrams of Fe in the catalyst per liter of solution.^f Milligrams of Fe leached after the reaction per liter of solution.

activity per site. Thus, although, it was concluded [133] that zeolite Y (Si/Al 2.6) was the most efficient, this catalyst does not reach the highest intrinsic activity of the Fe^{3+} site, but the data reflect only the higher iron content.

Ovejero et al. [135] addressed the wet peroxidation of phenolic solutions over different iron-containing zeolitic materials. The main results are displayed in Table 7. The catalyst series was prepared according to different procedures: hydrothermal crystallization of either xerogels (Fe-TS-1 samples) or basic hydrogels (Fe-ZSM5 and Fe-silicalite) and ion exchange (Fe-NaY, Fe-USY, and Fe-ZSM5). Even though the TOC reduction efficiency for directly

obtained xerogels containing iron is lower than iron exchanged zeolites, the leaching of Fe species is clearly reduced for those materials synthesized in this way (Fe-TS-1, 1.18 wt.% Fe). These results confirm that the direct synthesis gel with a moderate Fe content in the synthesis mixture allows active species to be incorporated into the zeolitic framework more strongly bonded than by ion exchange [135].

The following Table 8 compiles some other results that have been reported using metal exchanged zeolites as heterogeneous Fenton catalysts for the degradation of different probe molecules (phenol, Rhodamine 6G, Methyl Orange 6G, KN-R, methyl tert-butyl

Table 8Metal exchanged zeolites as Fenton catalyst for wet peroxidation in presence of H_2O_2 .

Catalyst	Catalytic activity		Reaction conditions	Ref.
	Substrate conversion (%)	TOC decrease (%)		
FeY ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5) (2.76 wt.% Fe)	>99.9 color ^b >74.2 COD ^b	66.8	Catalyst 1 g L ⁻¹ , 0.052 mM Reactive Yellow 84, 20 mM H_2O_2 , pH 5, 50 °C, 2 h reaction time as above	[133]
FeY ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 11.5) (1.69 wt.% Fe)	97.8 color >74.2 COD	51.6	as above	
FeY ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 80) (0.56 wt.% Fe)	78.8 color 38.6 COD	10	as above	
Cu/ZSM5 (1.62 wt.% Cu)	>90	<30	Catalyst 0.1 g L ⁻¹ , 10 mM phenol, 100 mM H_2O_2 , 80 °C, 3 h reaction time	[136,137]
Cu/ZSM5 (2.75 wt.% Cu)	>90	>30	Catalyst 0.6 g L ⁻¹ , as above	
Cu/ZSM5 (3.24 wt.% Cu)	>90	>35	Catalyst 0.6 g L ⁻¹ , as above	
Fe-ZSM5 (1.67 wt.% Fe)	100	>80	Catalyst 1 g L ⁻¹ , 0.21 mM Rhodamine 6G, 50 °C, 180 mM H_2O_2 (addition at 82 mmol h ⁻¹), pH ₀ 6, 1.3 h reaction time Catalyst, 1 g L ⁻¹ , 0.31 mM Methyl Orange 6G, 50 °C, 161 mM H_2O_2 (addition at 82 mmol h ⁻¹), pH ₀ 6.	[138]
Fe/ZSM5 (prepared by coprecipitation)	90	nd ^a	Catalyst 4 g L ⁻¹ , 0.4 mM Reactive Brilliant Blue KN-R, 30 mM H_2O_2 , pH 2.5, 0.33 h reaction time	[139]
Fe/ZSM5 (2.2 wt.% Fe)	~96 (3.9 h) ~96 (1.5 h) ~96 (0.6 h) ~96 (4 h)		Catalyst 25 g L ⁻¹ , 1.13 mM MTBE, 29.4 mM H_2O_2 , pH 7 (maintained constant). as above, but 55.9 mM H_2O_2 as above, but 176.5 mM H_2O_2	[140]
Fe-β (1.3 wt.% Fe)	40 of total phenols ^b 30 COD 59 color	28	as above	
Fe-β (Si/Al 50; Fe/Al: 1.19)			Catalyst 0.5 g L ⁻¹ , 20 mM H_2O_2 , pH 5.2, 28 °C, 12 h reaction time	[141]
Fe-ZSM5 (2.4 wt.% Fe)	66	35	Catalyst 16 g L ⁻¹ , 0.012 mM lignin, 3 M H_2O_2 , pH ₀ 3, 25 °C, 5 h reaction time	[144]

Table 8 (Continued)

Catalyst	Catalytic activity		Reaction conditions	Ref.
	Substrate conversion (%)	TOC decrease (%)		
Phenol hydroxylation using metal exchanged zeolites ^c				
CuNaY (1.56 wt.% Cu)	44.9	42.5% CAT/16.7% HQ/1.6% BQ	Catalyst 0.2 g, 2 g phenol (21.3 mmol), 2.4 g H ₂ O ₂ (30 wt.%; 21.3 mmol), 60 mL H ₂ O, 60 °C, 3 h reaction time	[142]
CuNaY (2.39 wt.% Cu)	45.3	43.6% CAT/18.3% HQ/1.0% BQ		
CuNaY (3.38 wt.% Cu)	50.3	50.3% CAT/22.3% HQ/2.1% BQ	HCl (0.01 M) enhances phenol conversion and selectivity towards CAT and HQ	
CuNaY (3.61 wt.% Cu)	56.2	41.9% CAT/19.4% HQ/1.0% BQ		
CuNaY (3.94 wt.% Cu)	66.5	30.0% CAT/14.5% HQ/1.0% BQ	Catalyst (2 g, fixed-bed), 70 °C, 4.0 h ⁻¹ weight hourly space velocity based on phenol, phenol/H ₂ O ₂ molar ratio = 3, water/phenol weight ratio = 4.5, 4 h time on stream	[143]
CuHY (1.08 wt.% Cu)	49.3	50.4% CAT/21.8% HQ/2.3% BQ		
CuUSHY (0.26 wt.% Cu)	15.2	45.1% CAT/15.7% HQ/18.0% BQ		
5CuHβ (1.05 wt.% Cu)	49.3	51.1% CAT/18.8% HQ/3.0% BQ		
CuHZSM5 (1.04 wt.% Cu)	47.0	8.8% CAT/4.2% HQ/1.5% BQ		
NaY	0.3	0.0% CAT/0.0% HQ/0.0% BQ/100% others		
Co-NaY (2.4 wt.% Co)	0.7	0.0% CAT/14.7% HQ/25.1% BQ/60.2% others		
Fe-NaY (2.1 wt.% Fe)	19.7	39.5% CAT/16.9% HQ/17.0% BQ/26.6% others		
Fe,Co-NaY (1.9 wt.% Fe, 1.8 wt.% Co)	21.8	44.8% CAT/16.5% HQ/12.6% BQ/26.1% others		
TS-1	7.4	15.9% CAT/66.9% HQ/6.4% BQ/10.8% others		

^a Not determined; nd.^b In these cases has been indicated the conversion of the specified parameter.^c When the term "Hydroxylation" is in the catalytic activity column indicates that Fenton reaction has been used as a synthetic method in order to obtain desirable products. In those cases, substrate conversion, as well as selectivity for the reaction products at the same time is indicated. CAT: Catechol; HQ: hydroquinone; BQ: benzoquinone.

ether (MTBE), lignine, Reactive Yellow 84) as well as for phenol hydroxylation [133,136–144].

9.2.3. Metal complexes encapsulated in zeolites

Complex encapsulation in zeolites has been a frequent strategy to develop active Fenton-like catalysts. One of the most studied metal complex encapsulated in zeolites with active metals in order to develop Fenton chemistry has been those based on salen ligand (SalenH₂) and derivatives (H₂Salpn, H₂Saldien, H₂hybe) (see Fig. 19) [145–149]. The term Salen corresponds to the compound formed from the condensation of ethylenediamine with salicylaldehyde. These bulky complexes can be synthesized inside the zeolite micropores by ship-in-a-bottle synthesis in which starting from precursors, that can diffuse through the pore apertures, the final complex is obtained and becomes permanently immobilized inside the cages of tridirectional zeolites [150].

Using metal salen complexes encapsulated in zeolites several reactions including H₂O₂ decomposition [145], phenol peroxidation [145–149] have been studied.

Apparently, encapsulation in zeolite-Y increases the stability of the active salen metal complex. One of the main drawbacks of salen complexes is the instability of the ligand towards hydrolysis

an oxidation. Salen ligands are easily hydrolyzed to the diamine and salicylaldehyde components. Fortunately, the stability of salen increases remarkably when the metal complex is formed. Nevertheless, the long term activity of the salen complexes is limited by the instability of the salen moiety. In this regard, phthalocyanines (Pc) are considerably more stable than salen and for this reason they are preferable ligands for the development of oxidation catalysts [151].

Sinha and Seelan reported [152] the higher activity and selectivity of CuPc-Y for phenol hydroxylation using H₂O₂ towards the corresponding CoPc-Y and VPC-Y (see Table 9 and Fig. 20).

Table 9 compiles some other results that have been reported using metal complex encapsulated zeolites for phenol hydroxylation [146–149,152].

10. Mesoporous silicas

In addition of layered aluminosilicates and microporous zeolites, mesoporous silicas have also been widely used for ion exchange and catalyst support [117]. The first mesoporous silicas reported were MCM materials from MOBIL [153,154]. The most studied material of this series has been MCM-41 whose structure is

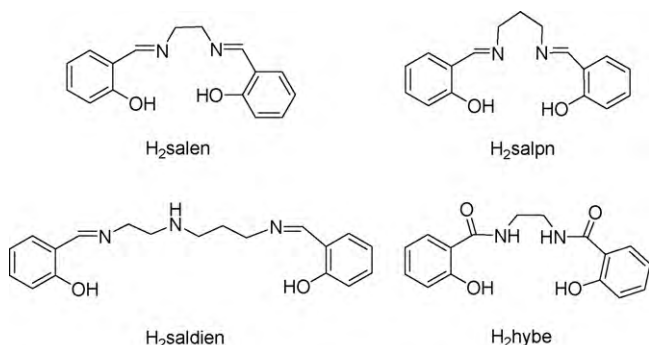


Fig. 19. Structure of O,O,N,N complexes derived from ortho hydroxy benzaldehyde.

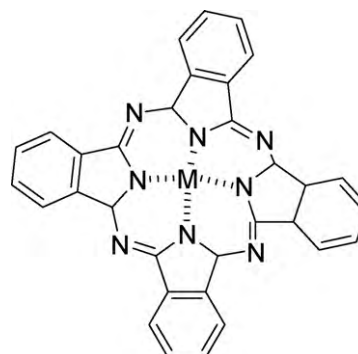


Fig. 20. Phthalocyanine complex with a metal (M).

Table 9
Metal complex encapsulated zeolites as heterogeneous catalysts for phenol hydroxylation.

Catalyst	Catalytic activity		Reaction conditions	Ref.
	Conversion (%)	Selectivity (%)		
Cr ³⁺ (salpn)-zeoliteY	~16	71.8.CAT/31.2.HQ	Catalyst 0.025 g, 4.7 g phenol (50 mmol), 1.2 g H ₂ O ₂ (30%; 10.6 mmol), pH (not indicated), 80 °C, 5 h reaction time	[146]
Fe ³⁺ (salpn)-zeoliteY	~24	68.8.CAT/27.2.HQ		
Bi ³⁺ (salpn)-zeoliteY	~6	91.6.CAT/ < 10.HQ		
Ni ²⁺ (salpn)-zeoliteY	<5	50.0.CAT/ < 20.0.HQ		
Zn ²⁺ (salpn)-zeoliteY	<5	90.0.CAT/ < 10.0.HQ		
Cr ³⁺ (saldien)-zeoliteY	~45	68.9.CAT/28.9.HQ	Catalyst 0.025 g, 4.7 g phenol (50 mmol), 5.67 g H ₂ O ₂ (30%; 50 mmol), 2 mL CH ₃ CN, 80 °C, 6 h reaction time	[147]
Fe ³⁺ (saldien)-zeoliteY	~30	80.0.CAT/16.7.HQ		
Bi ³⁺ (saldien)-zeoliteY	~33	84.8.CAT/12.1.HQ		
Zn ²⁺ (saldien)-zeoliteY	51.3	67.4.CAT/32.6.HQ	Catalyst 0.025 g, 4.7 g phenol (50 mmol), 5.67 g H ₂ O ₂ (30%; 50 mmol), 2 mL CH ₃ CN, 80 °C, 6 h reaction time	[148]
Ni ²⁺ (saldien)-zeoliteY	50.2	68.1.CAT/31.9.HQ		
Cu ²⁺ (saldien)-zeoliteY	46.0 (6 h)	68.3.CAT/31.7.HQ		
Fe(hybe)-zeoliteY	43.5	88.0.CAT/12.0.HQ	Catalyst 0.025 g, 4.7 g phenol (50 mmol), 5.67 g H ₂ O ₂ (30%; 50 mmol), 2 mL CH ₃ CN, 80 °C, 6 h reaction time	[149]
Cr(hybe)-zeoliteY	32.8	90.0.CAT/10.0.HQ		
Bi(hybe)-zeoliteY	30.6	85.0.CAT/15.0.HQ		
CuPc-Y (0.6 wt.% Cu)	35.0	62.9.CAT/28.5.HQ/8.2.BQ/0.2.others	Catalyst 0.1 g, 1 g phenol (10.6 mmol), 1.2 g H ₂ O ₂ (30%, 10.6 mmol), 20 g H ₂ O, 75 °C, 12 h reaction time	[152]
CoPc-Y (0.6 wt.% Co)	30.5	61.7.CAT/28.7.HQ/8.9.BQ/0.6.others		
VPc-Y (0.6 wt.% V)	25.2	65.4.CAT/16.1.HQ/14.9.BQ/3.7.others		

CAT: Catechol; HQ: hydroquinone; BQ: benzoquinone. See Fig. 19 for codes and structures of the Schiff base ligands.

formed by an array of parallel hexagonal channels of about 3.5 nm size. Periodic, structured mesoporous silicas rank at the top of the list of the most porous materials reaching values over 1000 m² g⁻¹ and 1 cm³ g⁻¹. They are typically prepared by using a long chain quaternary trimethylammonium ion as structure directing agent. In spite of the favourable properties of MCM-41 in terms of large surface area and porosity, numerous reports have shown that due to the wall thickness the structure of MCM-41, as determined by powder XRD, collapses upon long term storage in the presence of moisture or by stirring in aqueous solution [155]. Thus, it appears that MCM materials may not be most appropriate for their use in water.

An analogous mesoporous silica that is considerably more robust than MCM-41 against moisture and water is SBA-15 [156–159]. Typically the pore size of SBA-15 is around 10 nm that is significantly larger than the common MCM-41 pore size synthesized using cetyl trimethyl ammonium bromide (CTAB) as structure directing agent. Among the reasons of the higher stability it has been proposed that the main one is the wall thickness of the of SBA-15 silica that is significantly larger than those to MCM-41 [156,159].

The large structural stability of SBA-15 allows its use in aqueous suspension without loss of its mesoporosity. It has been reported [160] that iron oxide nanoparticles incorporated inside alumina-coated SBA-15 exhibits high activity as Fenton catalyst for the degradation of reactive black 5 dye (see structure in Fig. 21) and substituted phenol. The key point of the activity was the lining of the internal mesoporous surface of SBA-15 by a thin alumina layer as determined by comparing the performance of an analogous material in where iron oxide nanoparticles were included in SBA-15. Iron oxide was incorporated by impregnating mesoporous SBA-15 or alumina-coated SBA-15 with iron chloride followed by calcination in air at 300 °C. The iron content was about 12 wt.%. The coating of the inert SBA-15 walls with alumina was achieved by adsorbing AlCl₃ into SBA-15 until the silica-alumina ratio was 3 and subsequently submitting the aluminium chloride impregnated SBA-15 at 550 °C in air.

Iron nanoparticles supported on alumina-coated SBA-15 were found to perform efficiently in the degradation of reactive black 5 (100 mg L⁻¹) at 25 °C and pH 4.1 using 5 mM solution of H₂O₂ and 0.2 g L⁻¹ of iron-containing catalyst [160]. Fig. 22 shows a comparison of the catalytic activity of iron oxide on SBA-15 depending on the wall coating with alumina. Iron supported on aluminium-coated SBA-15 also exhibits high catalytic activity for the decomposition of H₂O₂ under the same conditions as those used for the reactive black 5 decoloration (see Fig. 22). Control experiments show that neither pure SBA-15 nor alumina-coated SBA-15 themselves exhibit any detectable activity for those processes. Using p-chlorobenzoic acid as probe molecule it has been proposed that the degradation/decomposition in the presence of iron nanoparticles supported on alumina-coated SBA-15 is due to generation of hydroxyl radicals.

Two concurrent factors have been suggested to explain why alumina coating improves the efficiency as catalyst of the resulting materials [160]. Considering that aluminium can be either tetrahe-

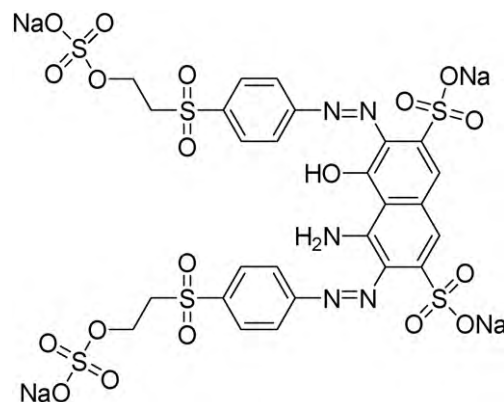


Fig. 21. Chemical structure of Reactive black 5.

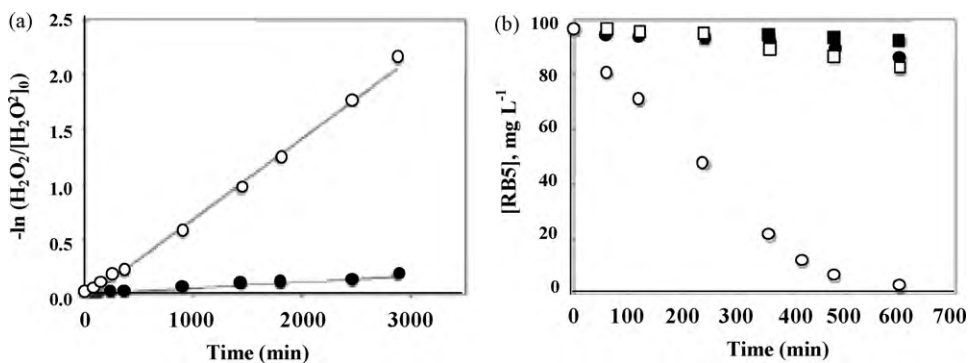


Fig. 22. (a) First-order fit of H₂O₂ decomposition for iron oxide nanoparticle inside SBA-15 (●) or alumina-coated SBA-15 (○); (b) Degradation of RB5 dye with (■) hematite, (□) magnetite, (●) iron oxide nanoparticle inside SBA-15 and (○) alumina-coated SBA-15 (figure taken from ref. [160]).

drally or octahedrally coordinated with oxygen atoms, each of these two species would contribute positively in a different way. On one hand, tetrahedral aluminium will introduce negative charges on the SBA-15 surface that by ion exchange will locate many Fe³⁺ ions in the walls. This large population of Fe³⁺ will act in the calcination as seeds for iron nanoparticles. It is known that the larger the number of seeds, the smaller the size of the nanoparticles. In fact the small particle size of iron oxide in alumina-coated SBA-15 as compared to the analogous SBA-15 was experimentally confirmed by powder XDR and TEM of the solids. In XDR the peaks corresponding to iron oxide became broader and less intense as the size of the nanoparticles decreases. The different particle size can also be assessed by TEM where the presence of iron oxide nanoparticles could be observed in SBA-15 but not in alumina-coated SBA-15.

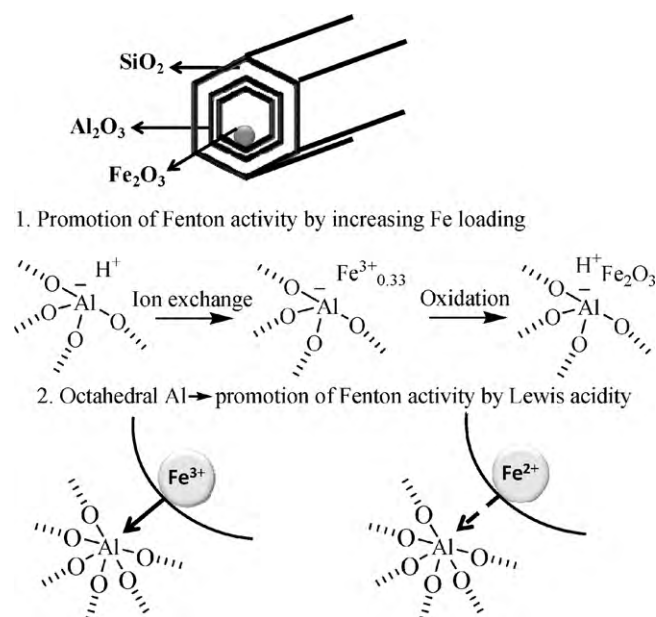
The second factor that enhances the catalytic performance of iron nanoparticles inside mesoporous silica when alumina is lining the channels is the Lewis acidity arising from octahedral aluminium [160]. In one of the mechanistic proposals for H₂O₂ decomposition on the surface of iron, the oxidation state should interconvert between +2 and +3 in a cyclic way. In this catalytic cycle, oxidation of ferrous ions by H₂O₂ is fast and does not require any catalyst but reduction of ferric ions by H₂O₂ is slow and can be promoted by the presence of Lewis acid sites. Apparently the role of octahedral aluminium promoting the activity of iron nanoparticles embeded on mesoporous silica lined by alumina is to attract electron density from the neighbour iron oxide nanoparticles stabilizing the +3 oxidation state. Scheme 4 summarizes the proposal.

Using several consecutives [161] cycles of incipient wetness impregnation of equimolar concentrations of manganese and iron nitrates on silica gel, followed by drying at 100 °C and a final calcination under nitrogen atmosphere at 800 °C a nanosized MnFe₂O₄ spinel supported on commercial silica gel has been prepared. These manganese ferrite nanoparticles can be removed from the silica support by dissolution of the silica phase with a 2 M NaOH solution. The overall process consists on the filling of silica gel mesopores by infiltration with a solution of Mn²⁺ and Fe³⁺, subsequent formation of the nanoparticles on the silica matrix and final digestion of the silica. In this way working with commercial silica gel of 340 m² g⁻¹ specific surface area MnFe₂O₄ with 93 m² g⁻¹ and about 13 nm average particle size can be easily prepared. The catalytic activity of this nanosized MnFe₂O₄ for the decomposition of H₂O₂ was examined at pH of 6 and 13 [161]. Similar catalytic activity was observed for these two pH values and, importantly, no leaching of iron into the solution was detected. The material was highly active, being able to effect the total decomposition of a 3 M H₂O₂ solution in 5 min using 800 mg of ferrite per liter of solution. However, it was found that the activity of the material is strongly dependent on the presence of residual silica that has been incompletely removed by the strong alkali treatment. Therefore it was concluded

that even though the initial activity of silica supported MnFe₂O₄ can be lower than that of unsupported MnFe₂O₄, the supported material is advantageous because it simplifies the preparation procedure and, at long term, should reduce the aggregation causing the catalytic deactivation of nanosized particles.

The resulting material consisting on MnFe₂O₄ supported on silica is similar to the previously commented iron oxide nanoparticles incorporated on mesoporous silica covered with an alumina layer [161]. A comparison of the catalytic activity for H₂O₂ decomposition between these two materials has shown that MnFe₂O₄ even without dissolution of the silica matrix is far more active than iron oxide embedded on alumina-coated mesoporous silica (see Fig. 23). One reason for this higher activity of the silica supported MnFe₂O₄ could be the promoting effect of manganese on the activity of iron oxide and therefore it would be of interest to perform a deeper study about how the presence of manganese or other transition metals influences the decomposition of H₂O₂ in these systems. One additional advantage of working with all these iron oxide materials is that being ferromagnetic they can be recovered from the reaction solution by applying a magnetic field.

In any case, to prove the use of these iron oxides as Fenton catalysts in addition of H₂O₂ decomposition the different catalytic



Scheme 4. Pictorial illustration of iron oxide supported on alumina-lined SBA-15 and influence of tetrahedral and octahedral Al on the catalytic activity of supported iron oxide.

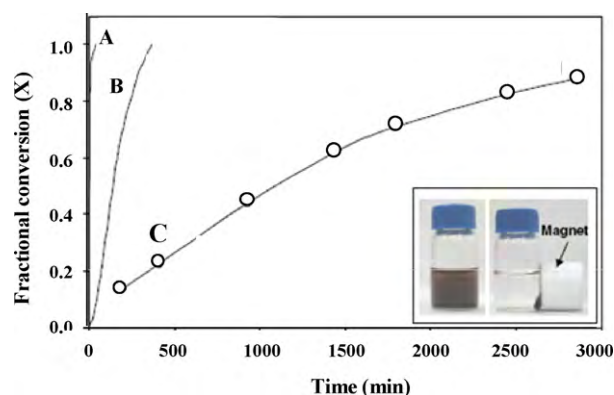


Fig. 23. Variation of the H_2O_2 decomposition with time for the MnFe_2O_4 nanoparticles (A), $\text{MnFe}_2\text{O}_4/\text{SiO}_2$ (B) and alumina-coated SBA-15 (active phase 0.2 g L^{-1} , $[\text{H}_2\text{O}_2] = 5 \text{ mM}$) [160] (C). Time values to achieve the highest conversion degrees: (A) 0.98 in 33 min; (B) 0.99 in 360 min; (C) 0.88 in 2858 min. Inset: illustration of the magnetic separation of nanoparticles from the liquid media (figure taken from ref. [161]).

activity for phenol degradation or some other Fenton reaction should have been determined for the various iron containing silica supported materials. Considering the array of pathways available for H_2O_2 decomposition it may happen that the most active catalyst for H_2O_2 decomposition is not the one that generates hydroxyl radicals with the highest efficiency. Therefore, only disappearance H_2O_2 , even being as important as it is, is not a valid reaction test to ensure the occurrence of Fenton chemistry.

The following Table 10 compiles some other results that have been reported using mesoporous silicas as heterogeneous catalysts for the Fenton reaction using H_2O_2 as oxidant [46,47,49,56,162–167].

11. Prospects and concluding remarks

The Fenton reaction is one of the most important processes for water and soil remediation, particularly when the concentration of pollutants is not high and the cost of consumed H_2O_2 makes the treatment affordable. Development of heterogeneous catalysts to replace soluble iron salts increases considerably the attractiveness of the process, particularly if it serves to overcome pH limitations and can be performed at room temperature or mild conditions.

Table 10

Mesoporous silicas as catalyst for the Fenton reaction using hydrogen peroxide.

Catalyst	Catalytic activity		Reaction conditions	Ref.
	Substrate conversion (%)	TOC decrease (%)		
MCM-41 support	~86	nd ^a	Catalyst 2 g L^{-1} , 1 mM phenol, 1 mM H_2O_2 , 80°C , 0.2 MPa (autogenous pressure), 5 h reaction time, at pH 3	[46]
Mn(II)-(by impregnation method)-MCM-41 (1.13 wt.% Mn)	~92	nd	as above, but pH 6	
	~95	nd	as above, but pH 9	
	~89	nd	Catalyst 2 g L^{-1} , 1 mM 2-chlorophenol, 1 mM H_2O_2 , 80°C , 0.2 MPa (autogenous pressure), 5 h reaction time, at pH 3	
	~92	nd	As above, but pH 6	
Fe-MCM-41 (Si/Fe = 25)	~85	nd	As above, but pH 9	[49]
	~70	nd	Catalyst 2 g L^{-1} , 1 mM 2-nitrophenol, 1 mM H_2O_2 , 80°C , 0.2 MPa (autogenous pressure), 5 h reaction time, at pH 3	
	~86	nd	As above, but pH 6	
	~91	nd	As above, but pH 9	
			Catalyst 4 g L^{-1} , 1 mM EDTA, 17 mM H_2O_2 (stoichiometric amount for mineralization), pH 4.5, 30°C , 4 h reaction time	[49]
			as above, but 50°C	
	nd ^a	~39	Catalyst 4 g L^{-1} , 1 mM oxalic acid, 1 mM H_2O_2 (stoichiometric amount for mineralization), pH 4, 30°C	
	nd	~50	as above, but 50°C	
	nd	~13		[162]
	nd	~20		
V-MCM-41	60	nd ^a	Catalyst 0.4 g L^{-1} , 0.02 mM Rhodamine Bextra, 4 mM H_2O_2 , pH 2.68, 2 h reaction time	
	60		As above, but pH 3.14	
	40		As above, but pH 6.15	
	15		As above, but pH 9.07	
SBA-15 support	12.5	nd	Catalyst 0.25 g L^{-1} , 2.2 mM ethanol, 441 mM H_2O_2 (through time intervals), initial pH 6.7, 25°C , 2 h reaction time	[47]
Mn ₃ O ₄ -SBA-15 (3.13 wt.% Mn) (by thermolysis of organic manganese (II) acetylacetonate in air)	~20	nd	As above, but 70°C	
	~12	nd	As above, but pH 9	
	~22	nd	As above, but pH 5.5	
	~27	nd	As above, but pH 3.5	
	~32	nd	As above, but pH 2	

Table 10
Mesoporous silicas as catalyst for the Fenton reaction using hydrogen peroxide.

Catalyst	Catalytic activity		Reaction conditions	Ref.
	Substrate conversion (%)	TOC decrease (%)		
Fe ₂ O ₃ -SBA-15 (16 wt.% Fe)	nd	~65	Catalyst 0.6 g L ⁻¹ , 10.6 mM phenol, 112 mM H ₂ O ₂ , 0.7 MPa (air pressure), 0.33 h reaction time, 100 °C, pH 2.5 (not buffered) As above, but pH 5.5 (not buffered) As above, but pH 7.0 (not buffered) As above, but pH 3.9 (buffered) As above, but pH 4.5 (buffered) As above, but pH 5.3 (buffered)	[56]
SBA-15	nd ^a	~12	Catalyst 0.6 g L ⁻¹ , 54.2 mM phenol, 29.4 mM H ₂ O ₂ , pH ₀ 5.5 (not buffered), 1 MPa (air pressure), 100 °C, 0.33 h reaction time	[163]
Fe ₂ O ₃ -SBA-15 (16 wt.% Fe)	nd	~58		
CuO-SBA-15 (20 wt.% Cu)	nd	~85		
Fe,Cu-SBA-15 (12.2 wt.% Fe; 7.5 wt.% Cu)	nd	~65		
Fe ₂ O ₃ -SBA-15 (19 wt.% Fe) (pellet form)			Catalyst 2.9 g (reactor dimensions: length 15 cm/internal diameter 1.2 cm), 0.86 g L ⁻¹ TOC (pharmaceutical wastewater), 15 mL h ⁻¹ flow rate, 10.8 g L ⁻¹ H ₂ O ₂ inlet (twice the stoichiometric to achieve complete mineralization), pH 3, 80 °C, over 55 h on stream Catalytic bed (75% catalyst/25% sodium bentonite) and synthetic methylcellulose polymer	[164]
Fe ₂ O ₃ -SBA-15 (14 wt.% Fe) (pellet form)	100 (on stream for 32 h)	~60 (on stream, until 22 h) ~35 (on stream, from 22 to 32 h)	Catalyst 2.9 g (reactor dimensions: L 15 cm/internal diameter 1.2 cm), 10.63 mM phenol, 60 mL h ⁻¹ flow rate (3.8 min residence time), 148.8 mM H ₂ O ₂ inlet (stoichiometric amount to achieve complete mineralization), pH ₀ 5.5, 80 °C	[165]
Phenol hydroxylation using mesoporous silicas as catalyst supports ^b MCM-41	0	0	Catalyst 0.05 g, 10 mmol phenol, 14.5 mmol H ₂ O ₂ , 30 ml H ₂ O, 80 °C, 2 h reaction time	[166]
Al-MCM-41 (Si/Al molar ratio 100)	36	62.0.CT/38.0.HQ		
Cu,Al-MCM-41 (Si/Al molar ratio 100; 1 wt.% 1Cu)	52	65.0.CT/35.0.HQ		
Cu,Al-MCM-41 (Si/Al molar ratio 100; 1 wt.% 2 Cu)	64	32.8.CT/36.0.HQ		
Cu,Al-MCM-41 (Si/Al molar ratio 100; 1 wt.% 4 Cu)	78	68.0.CT/32.0.HQ		
Cu,Al-MCM-41 (Si/Al molar ratio 100; 1 wt.% 6 Cu)	73	58.6.CT/41.4.HQ		
Cu-HMS	32.7	65.5CAT/30.6 HQ/3.9BQ	Catalyst 0.05 g, 10 mmol phenol, 20 mmol H ₂ O ₂ , 10.8 g H ₂ O, 60 °C, pH 7, 4 h reaction time	[167]
Cu-SBA-15 (immersion method)	41.9	65.5CAT/31.0HQ/4.0BQ		
TS-1	47.1	53.3CAT/45.7HQ/1.0BQ		
Cu-SBA-15	59.4	71.0CAT/26.2HQ/2.8BQ		
Cu-SBA-15	62.7	70.8CAT/27.6HQ/1.6BQ	As above, but 10 h	
Cu-SBA-15	65.5	76.8CAT/21.3HQ/1.9BQ	As above, but 5 h reaction time, 90 °C	

^a Not determined: nd.

^b When the term "Hydroxylation" is in the catalytic activity column indicates that Fenton reaction has been used as a synthetic method in order to obtain desirable products. In those cases, substrate conversion, as well as selectivity for the reaction products at the same time is indicated. CAT: Catechol; HQ: hydroquinone; BQ: benzoquinone.

We have presented in the previous sections data showing that layered and porous aluminosilicates and analogous double oxides containing iron, copper or even other transition metals exhibit catalytic activity for the Fenton process. However, as in any catalytic process the key point is efficiency in the use of reagent, in this case H₂O₂ to generate free hydroxyl radicals. This issue has been frequently ignored and, mostly, the disappearance of the model pollutant and/or reduction of total organic carbon have been the only parameters that have been studied. Optimization of H₂O₂ has also to be considered as one of the important parameters when ranking the efficiency of the solid catalysts. Thus, the current situation in this area does not allow drawing conclusions about the relative catalytic activity of the various solids tested. In addition to selec-

tivity in the conversion of H₂O₂, other parameters to be taken into account are the stability of the catalyst, the absence of leaching and aging of the catalytic sites, and the operation conditions including pH, temperature and amount of catalyst.

It can be anticipated that the use of the Fenton reaction will grow in the near future motivated by the logic environmental concerns and pollution remediation. Therefore, it can be predicted that future developments in this area will lead to a clarification of the present status with some materials established as lead catalysts in the field. The need to prepare single site catalysts in which the nature of the iron species supported on the solid are better defined should serve to prepare more efficient and general solid Fenton catalysts.

Acknowledgements

Financial support by the Spanish DGI (CTQ-2009-11586) is gratefully acknowledged. SN thanks to the Technical University of Valencia for a postgraduate research contract (Cantera Programme).

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